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Synthesis of new lewis acids
from semi-cyclic triarylboranes to 9-boratriptycene

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SYNTHESIS OF NEW LEWIS ACIDS: FROM SEMI-CYCLIC TRIARYLBORANES TO 9-BORATRIPTYCENE

Mémoire présenté pour l'obtention
du grade académique de Master Chimie «Chimie du Vivant et des Nanomatériaux» : Finalité Approfondie

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Synthèse de nouveaux acides de Lewis borés: De la synthèse de triarylboranes semi-cycliques à la synthèse du 9-boratriptycene

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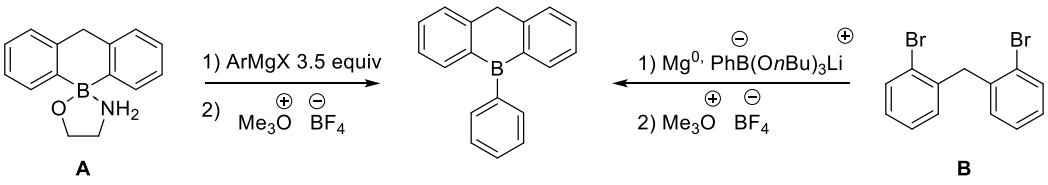
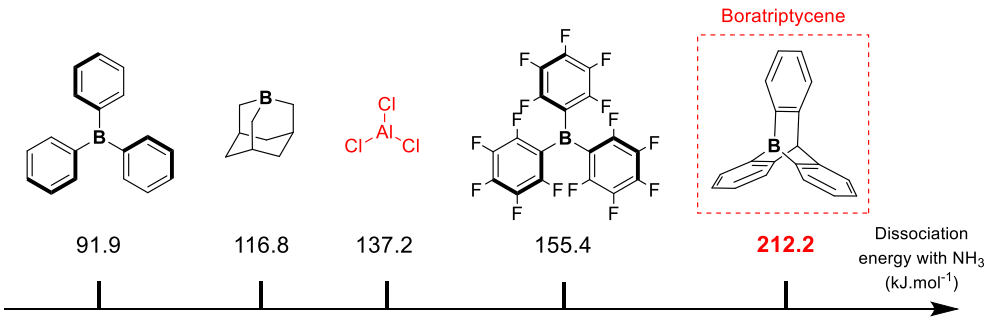
Résumé :

En raison de leurs propriétés chimiques, physiques et photophysiques, les composés organo-borés et en particulier les dérivés triarylboranes jouent un rôle central en sciences des matériaux, chimie supramoléculaire et en catalyse. Considérant l'intérêt croissant pour les dérivés borés en catalyse organique et en chimie des paires de Lewis frustrées, nous avons décidé de synthétiser une nouvelle classe d'acide de Lewis borés dérivant directement des triarylboranes, à savoir les triarylboranes semi-cycliques. Notre travail porte donc sur la synthèse et l'étude fondamentale de la structure et des propriétés électroniques de ces triarylboranes semi-cycliques. La synthèse de ces composés a été réalisée à partir d'un dérivé amino-borinate comme source de bore éléctrophile **A** ou par une procédure « one-pot » à partir de bis(2-bromophenyl)methane.



En parallèle de la synthèse de triarylboranes semi-cycliques, nous nous sommes intéressés à la synthèse du 9-boratriptycene. Ce composé possède structure de triptycene dans laquelle un atome de carbone en tête de pont a été substitué par un atome de bore. La particularité de ce composé est l'important caractère pyramidal de l'atome de bore qui lui confère des propriétés acide de Lewis exacerbées. Des études théoriques récentes ont mis en lumière l'extraordinaire potentiel de ce composé en tant qu'acide de Lewis ce qui nous a conduit à développer différentes voies de synthèses de ce composé.



Mémoire de master en Sciences Chimiques à Finalité Approfondie
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Promoteur: Prof. G. Berionni

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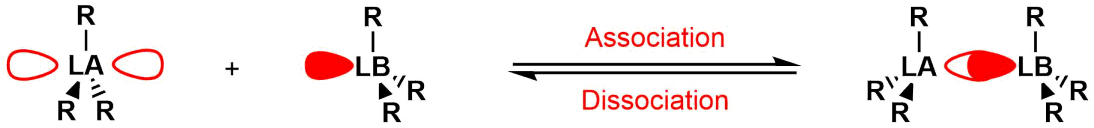
Contents

CHAPTER 1

Introduction

1.1 Lewis acids and bases

Any chemical species, atom, molecule or functional group, that can accept a lone pair of electron belong to the class of Lewis acids while any chemical species that can donate a lone pair of electron belong to the class of Lewis bases [1] . These generalized acidity and basicity concepts, introduced by G.N. Lewis in 1923, are fundamental for the understanding of the association of Lewis acids and bases [2]. These reacts together to form Lewis adducts in which the acid and base are linked together via dative covalent bond. To form this Lewis adduct, the electron density of the free lone pair of the Lewis base is transferred into the empty orbital of the Lewis acid which reduce the electron deficiency of the Lewis acid (Scheme 1.1) [3], [4].



Scheme 1.1: Formation of Lewis adduct.

This adduct is either irreversibly formed or can be dissociated by increasing the temperature or in presence of a stronger Lewis acid or base. In modern chemistry, most of the common Lewis acids are belonging to the group 13 element derivatives, such as $AlCl_3$, and are generally in oxidation state $+3$ [5]. Borane derivatives are the most common Lewis acids due to the electron deficiency of the central boron atom owing to the vacant p-orbital [4], [6].

1.2 Lewis acidity of trivalent boron derivatives

Boron derivatives are the archetypal Lewis acids derivatives. Due to the empty p orbital, the boron doesn't respect the octet rule and consequently presents an important electron deficiency. This Lewis acidity can be tuned considering the different substitution patterns on the boron atom. At first sight, it is important to note that trialkylboranes are more acidic than triarylboranes [6]. Indeed triethylborane is much more acidic than triphenylborane, which is due to the absence of retrodonation of the substituent into the p ortbital of the boron, increasing the electro-deficiency [6]. However, despite their stronger Lewis acidity, trialkylborane are not used for their Lewis acidic properties due to their highly sensitivity towards oxygen. Therefore, adding electrowithdrawing substituents on the boron atom seams to be a classical way to increase the electron deficiency and consequently the Lewis acidity, but this feature may sometimes be counterintuitive. The most classical example is the serie of halogen derivative boron compounds. It seem obvious that $\mathrm{BF_3}$ would be a stronger Lewis acid than $\mathrm{BCl_3}$ due to stronger electronegativity of the fluorine atom. Actually, $\mathrm{BCl_3}$ is much more acidic than $\mathrm{BF_3}$. Due to the similar size of the boron and fluorine atom, the p orbitals of fluorine and boron atom overlap perfectly which induces a π-electron donation into the boron p orbtital and decreases the electron deficiency of the boron atom (Figure 1.1) [7], [8] .

Figure 1.1: π-interaction between fluorine and boron atom and between chlorine and boron atom in $\mathrm{BF_3}$ and $\mathrm{BCl_3}$ respectively.

However, considering aryl borane derivatives, adding fluorine substituents on aryl groups remain one of the best way to increase Lewis acidity of the boron atom. Indeed, one of the most powerful boron Lewis acid is the tris(pentafluorophenyl) borane (BCF) in which all hydrogen atoms are replaced by fluorine atoms [6], [9]. However, this strategy remains limited. First, the replacement of all the hydrogen atoms by fluorine atoms might be counterproductive. As highlighted by Gilbert the presence of fluorine in the two *ortho*-position of each aryl substituent causes steric hindrance which decreases the Lewis acidity of the compound (Figure 1.2) [10].

Secondly, considering BCF, its Lewis acidity is similar to boron trifluoride but it is nearly impossible to increase significantly the amount of electro withdrawing substituents [6]. Furthermore, pefluorinated aryl rings may be sensitive to S_NAr reactions in presence of certain Lewis basis [11]. Another option to increase the Lewis acidity is the design of anti-aromatic systems such as 9-phenyl-9-borafluorene. In this system, the anti-aromaticity strongly increases the electron deficiency on the boron atom and consequently the Lewis acidity (Figure 1.3). However, due to the anti-aromaticity, such compounds

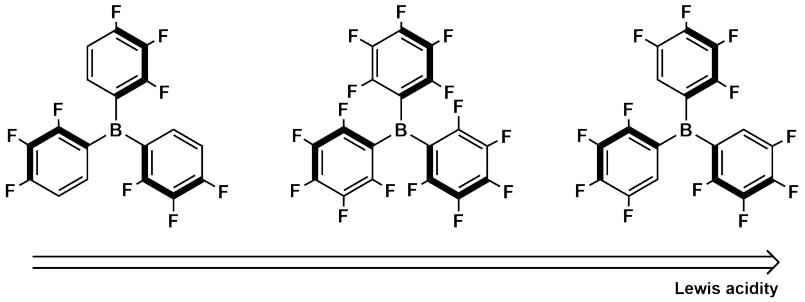


Figure 1.2: Decrease of the Lewis acidity $\mathrm{B(C_6F_xH_{y-x})}$ with fluorine in position 2- and 6-.

are highly sensitive towards moisture and unstable [12].

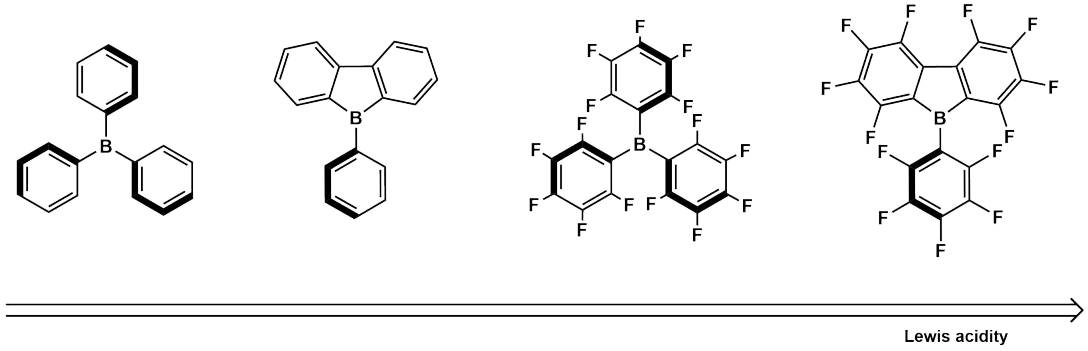


Figure 1.3: Influence of the anti-aromaticity on the Lewis acidity of triaryl borane.

The last option to improve the Lewis acidity of boron compounds, which is much less obvious, consists in constrain the boron atom in a pyramidal shape. Indeed, considering classical boron Lewis acids such as $B(Ph)_3$ or BCl_3, the boron atom and the three atoms attached lie in a completely planar environment with bond angles of $120°$ between the subsituants. When the Lewis acid reacts with the Lewis base to form the adduct, the molecule rearranges and the boron atom become tetrahedral. This rearrangement requires some energy to occur which impacts the Lewis acidity of the compound. The more energy is required, the less acidic the compound will be (Figure 1.4) [9], [13], [14].

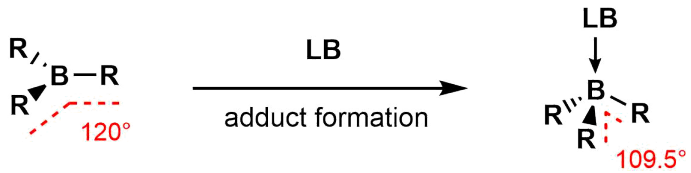


Figure 1.4: Deformation induced by the formation of the Lewis adduct.

To overcome this loss of energy, it is possible to insert the boron atom into a rigid structure to constrain its geometry into a pyramidal shape. Constrained in a pyramidal shape, the boron atom is closer from the tetrahedral shape of the Lewis adduct, consequently the rearrangement energy is decreased and the Lewis acidity is increased. Recent theoretical research highlighted the potential of the pyramidalisation of the boron atom to increase the Lewis acidity (Figure 1.5). Some of these compounds, such as1- boraadamantane, have already been synthesized but no application ensued so far [9].

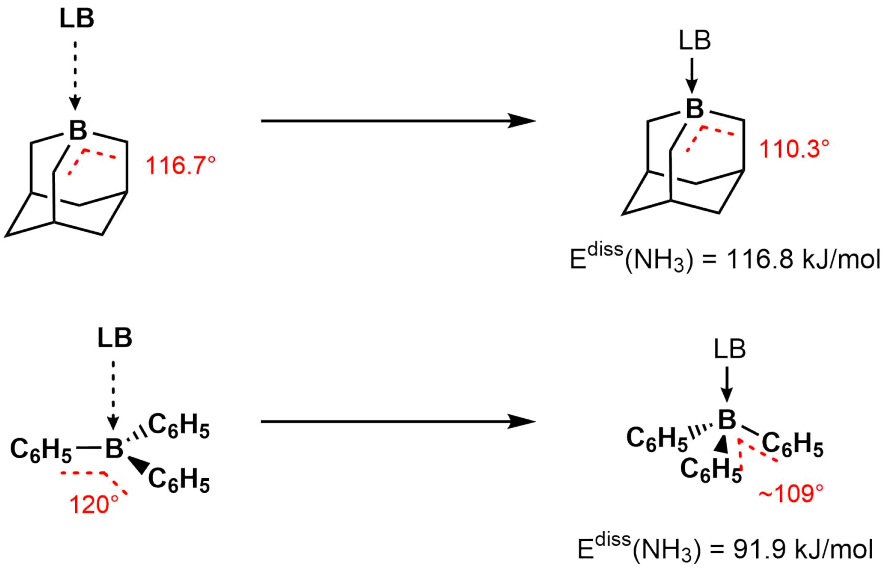


Figure 1.5: Deformation induced by the formation of the Lewis adduct in the 1-boraadamantane and triphenylborane [9], [15].

1.3 Quantification of the Lewis acidity

Whereas Brönsted acidity scale is based on the property of a compound to release a proton (H^+), it is important to define the Lewis acidity scale. The Lewis acidity scale is however not as universal as the Brönsted acidity scale due to the dependency on the type and size of the reference Lewis base. Indeed, the steric hindrance may play an important role in the apparent Lewis acidity of compounds which is not the case for Brönsted acids since the proton is the smallest entity. Nowadays, three different scales for estimation of the Lewis acidity of boron compounds are most widely used. The first method is based on the fluorine ion affinity, the more a substance as affinity for a fluorine ion, the more acidic it is. This method is purely computational and is expressed in terms of enthalpy of the reaction 1.1.

$$CF_3O^- + LA \rightleftharpoons COF_2 + LA{-}F^- \tag{1.1}$$

The major advantage of this method is the absence of deviation due to the steric hindrance, the fluoride anion being one of the smallest Lewis base, the steric hindrance is strongly limited. The major inconvenient of this method is the dependence on the calculation method used [1]. The two other methods are based on NMR spectroscopy. The Gutmann-Beckett method, which is the most popular, is based on the observed $^{31}\mathrm{P}$ NMR chemical shift of $\mathrm{Et_3PO}$ with two reference namely $\mathrm{Et_3PO}$ in hexane as the 0 point ($\delta = 41.0$ ppm) and $\mathrm{Et_3PO}$ in $\mathrm{SbCl_5}$ as the 100 point ($\delta = 86.1$ ppm) [1], [16]. The last method, developped by Childs and co-workers is based on the observed $^{1}\mathrm{H}$ NMR chemical shift of the proton $\mathrm{H_3}$ of crotonaldehyde in the presence of a Lewis acid. The two reference points of this method are the $^{1}\mathrm{H}$ NMR chemical shift of crotonaldehyde in $\mathrm{CDCl_3}$ or $\mathrm{CD_2Cl_2}$ as the 0 point ($\delta = 6.98$ ppm) and of crotonaldehyde in presence of $\mathrm{BBr_3}$ as the point 1 ($\delta = 1.49$ ppm) (Figure 1.6) [1], [17].

Figure 1.6: Structure of trethylphosphite used for Gutmann-Beckett's test (left) and crotonaldehyde used for Childs's test (right).

Those two NMR methods are commonly used but, as the fluorine ions affinity, depends on the calculation method used, those ones depend on the conditions of the analysis. The solvent, the temperature, the concentration, and even the NMR tube may influence the results of the experiments. Consequently, for a single Lewis acid, different values of chemical shift may be found in the literature. As example several δ values from Guttman-Becket analysis, from 65.9 to 72.5 ppm, may be obtained concerning triphenylborane [6]. Furthermore, in some cases the compounds compared are not soluble in the same solvent which preclude quantitative comparison. It is also important to note that the results obtained with Guttman-Beckett and Childs sometimes afford opposite results.

Another method may be relevant to evaluate the Lewis acidity of boron compounds and is based on the tetrahedral character of the boron atom. This method is called thetrahedral boron character index (THC) and is based on the tetrahedral character of the boron atom in a Lewis adduct. Indeed, a standard boron Lewis acid is found to be planar with bond angles of $120°$ between the substituents. When this boron Lewis acids forms a Lewis adduct with a base, a deformation is induced and the boron atom become tetrahedral, such as a carbon atom in a molecule of methane. The closer the angles between the substituents are from $109{,}5°$, the higher the THC is and the stronger the Lewis acid is (Figure 1.7) [14].

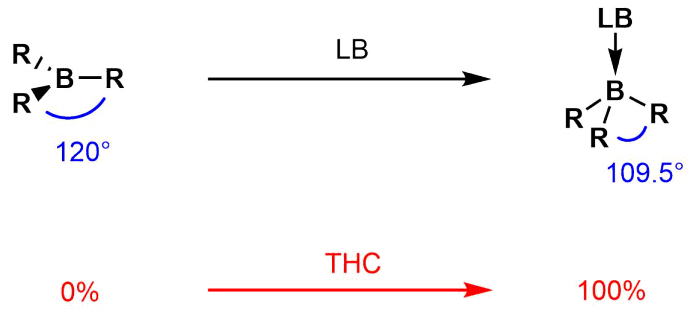
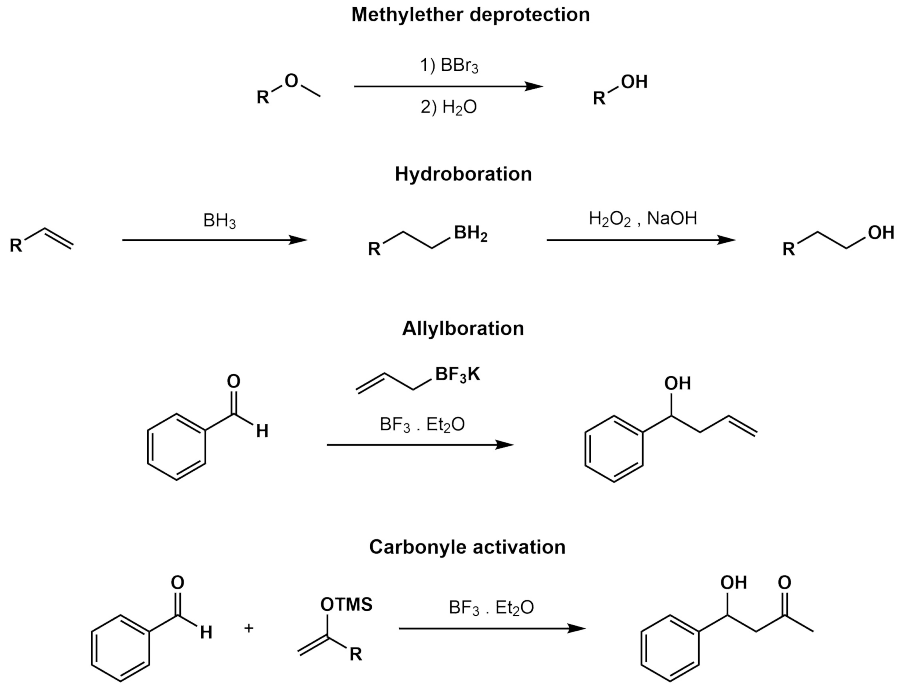


Figure 1.7: Change in the geometry of the boron atom induced by the formation of Lewis adduct.

The THC parameter constitute a efficient qualitative evaluation of the Lewis acidity. Actually, this remains an ideal representation, in the case of several strong boron Lewis acids, the THC parameter is upper than 100% which has no sense and consequently, any comparison may be difficult.

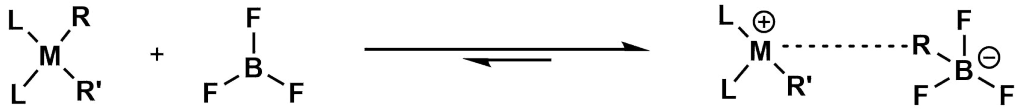
1.4 Application of boron Lewis acids

Boron Lewis acids are widely used in organic synthesis for the deprotection of methyl ethers in presence of boron tribromide, the hydroboration of alkenes in presence of borane, allylboration and activation carbonyles (Scheme 1.2).



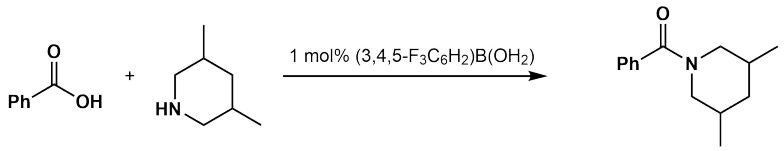
Scheme 1.2: Common applications of boron Lewis acids in organic synthesis.

Boron Lewis acids may also be used as catalysts and electrophilic boron sources such as trialkyborates. Their applications in catalysis are wide, all type of Lewis acids may find applications as catalyst from trihalogenoborane to triarylborane including their borinic and boronic forms. Trihalogeno borane such as boron trifluoride etherate are commonly used as co-catalyst in industrial processes, namely as co-catalyst for Ziegler-Natta catalyst (Scheme 1.3) [18], [19], [20] .

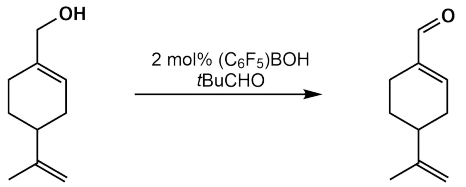


Scheme 1.3: Boron trifluoroborate as activator of Ziegler-Natta catalyst.

Aryl boronic acids found their major application in catalytic amidation reaction which has some importance in organic synthesis (Scheme 1.4) while diarylborinic acids found applications as catalysts in Mukaiyama aldol condensation or even in Oppenauer oxidations (Scheme 1.5) [20], [21], [22].

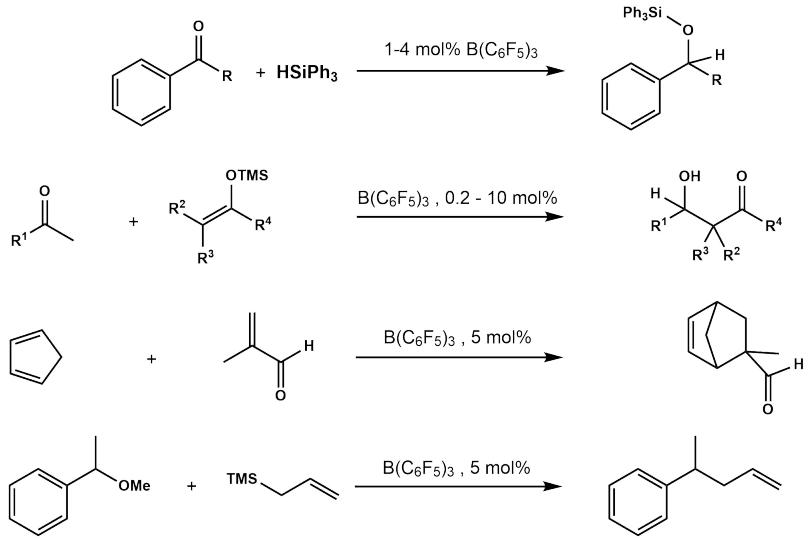


Scheme 1.4: Catalytic amidation in presence of arylboronic acid.



Scheme 1.5: Catalytic oppenauer oxidation in presence of diarylborinic acid.

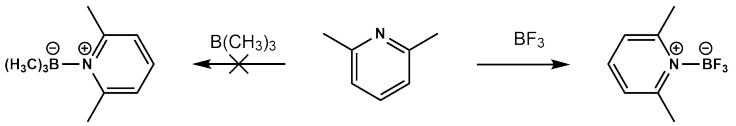
Boron Lewis acids showing the widest field of application are triaryboranes and especially tris-(pentafluorophenyl)borane. Since its first synthesis by Massey in 1963, this compound has attracted growing attention among synthetic chemists due to pecular properties and is cited in more than 4000 references. The major interesting properties are the good thermal and hydrolytic stability. Indeed, this compound decomposes at $270\,^{\circ}\mathrm{C}$ which allows to use it in a lot of different processes and to purify it by sublimation. The hydrolytic stability is an attractive feature compared with other common Lewis acids such as BF_3 and BCl_3 which decomposes rapidly in presence of water. These properties combined with a very strong Lewis acidity, between BF_3 and BCl_3 make this compound quite useful as catalysts in many organic reactions such as aldol type reactions, hydrosilylation, Diels-Alder reactions, allylation reactions, etc (Scheme 1.6). The last attractive feature is the steric hindrance on the boron atom which allowed the development of frustrated Lewis pair chemistry [20], [23], [24].



Scheme 1.6: Aldol-type, allylation, Diels-Alder and allylation of benzylic methoxyide reactions catalysed by $B(C_6F_5)_3$.

1.5 Frustrated Lewis pairs

Lewis acids and bases usually react together to form adducts. After the adduct formation, the base and the acid exhibit new properties and lose their basic or acidic properties. In 1942, H. C. Brown discovered that lutidine form a strong Lewis adduct with BF_3 but not with $B(CH_3)_3$ which is less Lewis acidic and bulkier (Scheme 1.7) .



Scheme 1.7: Reaction of lutidine with $B(CH_3)_3$ and BF_3.

Those observations led to the conclusion that sterically hindered Lewis acid and base do not form the Lewis adduct and may find an alternative pathway for reactivity. This stands for the first example of what is commonly called frustrated Lewis pair (FLP) (Figure 1.8).

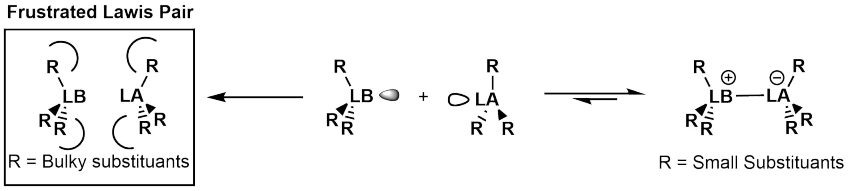
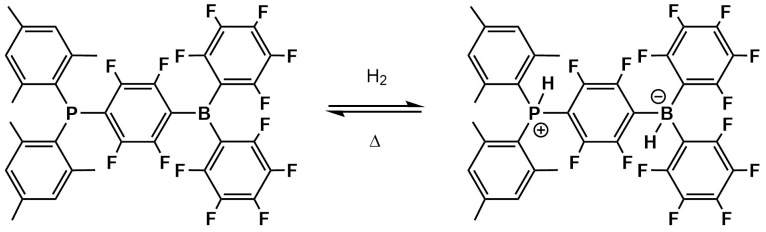


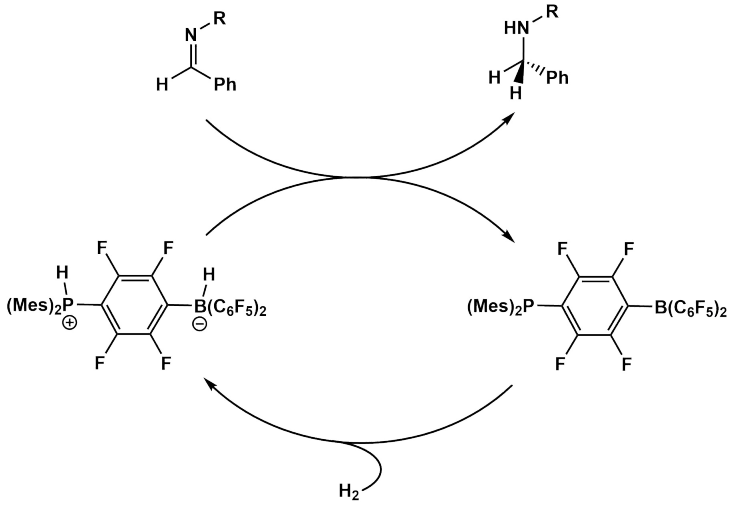
Figure 1.8: Concept of frustrated Lewis pair.

In 2006, D. W. Stephan demonstrate that an intramolecular FLP induces a reversible cleavage of molecular H_2 (Scheme 1.8) and in 2007 reported the same results using bulky phosphine and $B(C_6F_5)_3$ and led to the formation of phosphonium and hydridoborate while G. Erker reported the same results using an intramolecular ethylene-bridged phosphine/borane Lewis pair [11] [25], [26]. The work of Stephan and Erker highlighted that the combination of a bulky Lewis base and a bulky, electrophilic Lewis acid, instead of forming an adduct, could act in a cooperative pathway to activate small molecule and laid the foundation of frustrated Lewis pair chemistry.



Scheme 1.8: Hydrogen activation via frustrated Lewis pair.

Shortly after the discovery of metal-free activation of H_2 with frustrated Lewis pairs, it become important to find a way to use the activated hydrogen to make reactions. Considering the case of phosphine/borane FLP's, if the proton of the phosphonium and the hydride of the borate could be transferred to another molecule, the phosphine and borane could be regenerated and form a catalytic cycle. The first example of catalytic hydrogenation with FLP was carried out on imines in 2007 by Stephan and straight on aziridines (Scheme 1.9). During the following years, the hydrogenation of silyl enol ethers, some of non-functionilized alkenes and alkynes or even polycyclic aromatics were performed [27] [27], [28], [29], [30].



Scheme 1.9: Catalytic reduction of imine with frustrated Lewis pair.

Not only molecular hydrogen can be activated using FLP, other gases such as CO_2, N_2O of SO_2. In 2010, Piers and co-workers described the hydrosilylation of carbon dioxyde which allows to convert it into formic acid, formaldehyde, methanol or methane. Nowadays, the major actual deal with frustrated Lewis pair is the C-H activation [31],[32].

1.6 Non-planar boron Lewis acids

In 1974, Mikahilov reported the first synthesis of 1-boraadamantane which represent the first example of a non-planar borane incorporated in a cage shaped structure (Figure 1.9) [33]. However, its Lewis acidic properties have not been fully studied or compared with other compounds before the DFT study of Timoshkin in 2011 [9]. Despite the pyramidal character of the boron atom, the Lewis acidity reported by Timoskin turned out to be limited, stronger than triphenylborane but far weaker than BCF. However, with average C-B-C angle of $109.4°$, this compound highlight the effect of the pyramidalisation of the boron atom on the Lewis acidity. Surprisingly, although limited, this compound has never been used for its acidic properties and no application in catalysis have been reported so far.

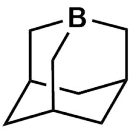


Figure 1.9: Structure of 1-boraadamantane.

30 Years later, Baba and co-wokers reported the synthesis of a caged shaped borate based on triphenolic methane. This compound presents a slight pyramidalisation of the boron atom with average C-B-C angle being $119.9°$. The pyramidalisation of the boron atom is present but negligible. Nevertheless, this compound show increased Lewis acidic properties compared to the open shaped equivalent (Figure 1.10). However this increased acidity is not due to pyramidalisation of the boron atom but to the poor conjugation between the oxygen and the boron atom which decreased the electron density on the boron atom inducing a higher Lewis acidity [34].

In 2006, Piers and co-workers reported the synthesis of borabarrelene and borabenzobarrelene from [4+2] cycloaddition on borabenzene adduct with pyridine (Figure 1.11). As an adduct with pyridine, the B-N bond length turned out to be the shortest ever observed. Average B-N distance being 1.650Å, the B-N distance in the borabenzobarrelene adduct with pyridine is $1{,}589$ Å. Furthermore, the average C-B-C angles turn out to be $104.0°$ which may be compared to the C-B-C angle in the BCF-pyridine complex, namely $111.0°$. Those structural parameters highlight the potential Lewis acidic properties of this new class of boron Lewis acids. However, those compounds have not been isolated in their trivalent form so far but as an adduct with a Lewis base [35].

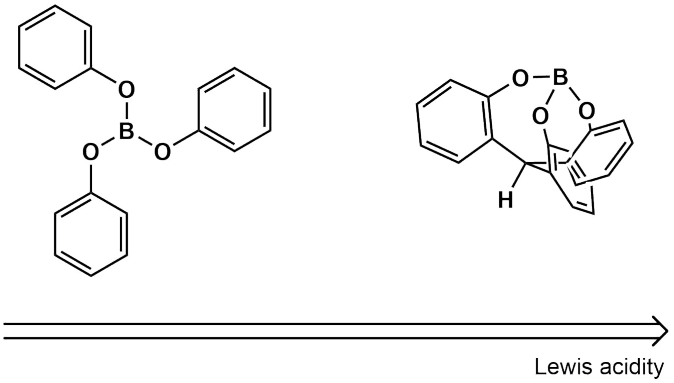


Figure 1.10: Lewis acidity of triphenylborate and its caged equivalent.

Figure 1.11: Structure of borabarrelene and benzoborabarrelene.

In 2018, Peters and co-workers and Sayamura and co-workers reported the synthesis of 9-phosphatriptycene-10-phenylborate (Figure 1.12). With a tetravalent boron atom, those compounds have not been synthesized for their Lewis acidic properties but as ligands for metals in organometallic chemistry. However, according to their experimental values, the average C-B-C angles is $104.4°$, which represent an strong pyramidalisation of the boron atom [36], [37]. This compound being a tetraaryl borate, those values can't be compared with the values of the benzoborabarrelene-pyridine adduct. However, those experimental values highlight the potential Lewis acidic properties of a boron atom incorporated into a triptycene scaffold, according to the DFT calculation reported by Timoshkin in 2011 [9].

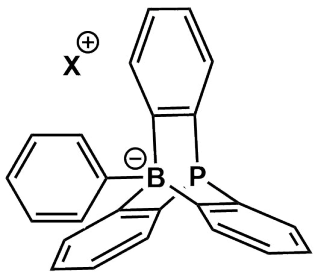
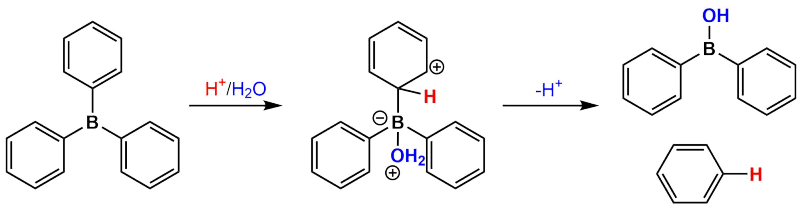


Figure 1.12: Structure of 9-phosphatriptycene-10-phenylborate.

Those few compounds constitutes the only examples of a pyramidalized boron atom incorporated into a caged shaped structure which highlight the lack of research in this domain. Furthermore, the major part of those compound having never been isolated with the trivalent boron atom, no complete experimental study concerning the effects of the pyramidalisation of the boron atom on the Lewis acidity have been performed so far.

1.7 Policylcic aromatic organoboranes

Due to their luminescent and semi-conductive properties, policyclic aromatic compounds are commonly used to design dyes and materials. Since 2000's, they have attracted increasing interest due to the discovery of remarkable optoelectronic properties driven by the incorporation of a boron atom in the structure [38], [39], [40], [41]. By connecting π conjugated systems with a boron atom, conjugation of the π system with the empty orbital p_z of the boron are allowed. This $p_\pi - \pi^*$ conjugation leads to the appearance of unique electronic and photophysical properties. It is often necessary to use hindered aromatic compounds, such as mesytyl, to increase their air and moisture stability [42]. For example, the triphenyl borane degrades itself within a few seconds in presence of water by protodeborylation (Scheme 1.10) [43], [44].



Scheme 1.10: Mechanism of protodeborylation

Polyaromactic boranes are also increasingly used as anion sensors. A fine tuning of the structure, the steric hindrance and the electronic properties make the boron atom only sensitive towards certain type of anion, fluoride or cyanide sensors being the most classical examples [45], [46]. Anion sensors are expected to show certain properties. Considering any triaryl borane, due to the planarity of the molecule, this one is completely conjugated and often coloured. The coordination of an anion such as fluoride to the boron atom should induce a pyramidalisation of the boron atom which induces a loss of conjugation in the molecule. The colour of the molecule then should change or disspear this should be measurable by spectrophotometry. The binding of the anion should be fast and quantitative for the method to be efficient (Figure 1.13).

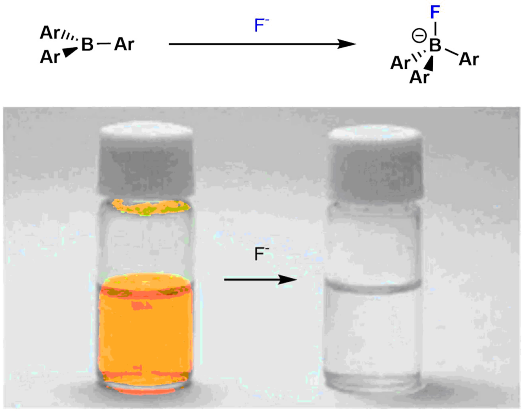


Figure 1.13: Colorimetric fluoride anion sensor

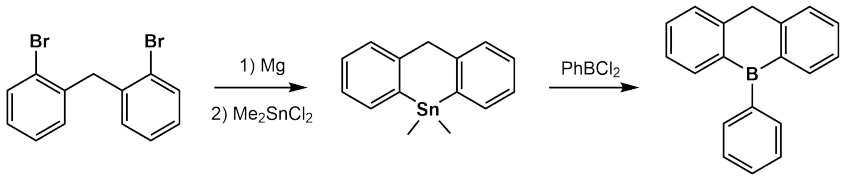
A major problem remains with this type of borane compounds, espacially the cyclic or semicyclic once : the synthesis. The classical synthesis of cyclic and semi-cyclic borane involves a lot of challenges, inert condition all along the synthesis, very high purity reagent and very toxic reagent. Furthermore, those synthesis are often carried out with overall poor yields. An increasing interest for these compounds combined with very difficult synthesis drew our attention in developing new and powerful synthesis of such semi-cyclic boranes.

CHAPTER 2

Synthesis of semi-cyclic triarylborane

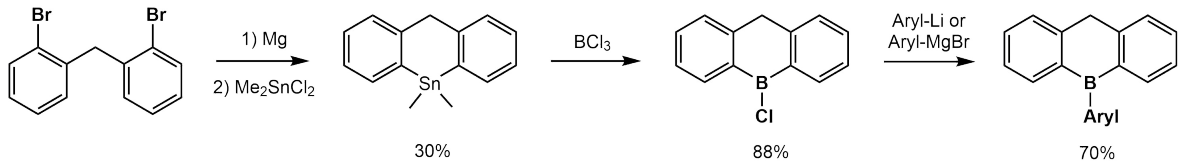
2.1 Introduction

In 1969, Jutzi described the first synthesis of a semi-cyclic triarylborane. Despite the availability of the starting materials, this two step synthesis involves highly toxic and unstable reagent. Furthermore, a high purity of the starting materials and intermediates is required to obtain the desired product. The yields of the products were not given by Jutzi and co-workers (Scheme 2.1) [47].



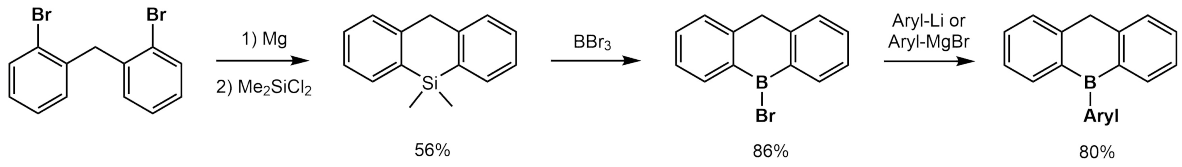
Scheme 2.1: First described synthesis of semi-cyclic triarylborane by Jutzi and co-workers in 1969 [47]

With the aim of modifying the aryl substituent on the boron atom, boron trichloride has been used instead of phenyl boron dichloride which allows the subsequent addition of an aryl lithium or magnesium bromide. If this strategy may open the route to the addition of electro-withdrawing aryl substituents, the use of unstable chloro boron reagent is still required (Scheme 2.2).



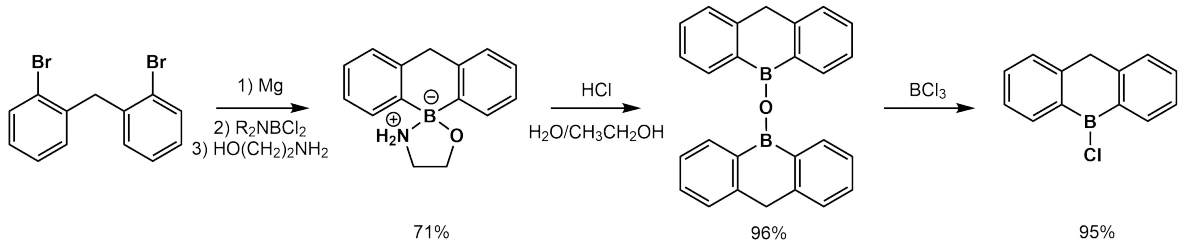
Scheme 2.2: Variant of Jutzi's semi-cyclic borane synthesis using boron trichloride

The previous synthetic pathway could also be performed using the silyl equivalent of dimethyltin dichloride which is considered less toxic, as described by Yamaguchi and co-workers (Scheme 2.3) [46].



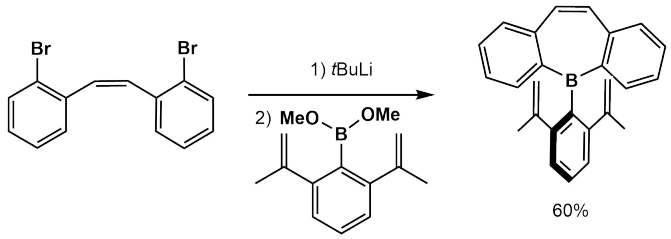
Scheme 2.3: Variant of Jutzi's semi-cyclic borane synthesis using dichlorodimethylsilane and boron tribromide

In 1970, Bickelhaupt tried to develop a new method to synthesize such semi-cyclic boranes avoiding organotin reagent. This strategy consists in the synthesis of 9-aminoethoxy-9,10-dihydro-9-boraanthracene, which is a borinic acid protected with ethanolamine, followed by deprotection and dehydration, to form the 9-hydroxy-9,10-dihydro-9-boraanthracene anhydride. Anhydride is then chlorinated on the boron atom using boron trichloride (Scheme 2.4) [48].



Scheme 2.4: Bickelhaupt synethesis of semi-cyclic borane

Very recently, Yamaguchi and co-workers described a direct synthesis of semi-cyclic triarylborane using dialkoxy aryl borane. Unfortunately, this strategy is limited to boron compound showing an important steric hindrance on the aryl substituent which has to be synthesized in an additional step (Scheme 2.5) [49].

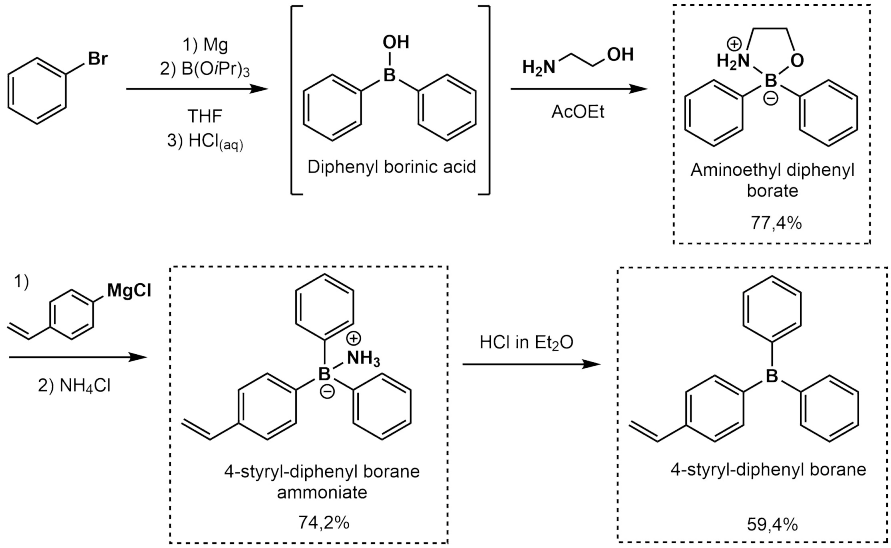


Scheme 2.5: Yamaguchi semi-cyclic arylborane synthesis

In the context of frustrated Lewis pair chemistry and Lewis acid catalysis, new type of boron based Lewis acids are still on demand. Only few semi-cyclic triarylboranes have been synthesized so far and their Lewis acidic properties as well as their stability toward ambient conditions have not been studied. Following those considerations, our first project deals with the aim of the synthesis of a new class of semi-cyclic triarylboranes and the study of their Lewis acidic properties as well as their stability compared with common triarylboranes such as triphenylborane.

2.2 Context of the research and preliminary results

The synthesis of 4-strytyl-diphenylborane described by Wang and co-workers constitutes the starting point of our work [50]. This method presents some interesting points, notably the direct addition of a Grignard reagent over an ethanolamine protected borinic acid and, additionaly, a quenching with saturated ammonium chloride inducing the formation of a protected 4-styryl-diphenyl borate ammoniate. The ammonia is then removed using hydrochloric acid in diethyl ether (Scheme 2.6).

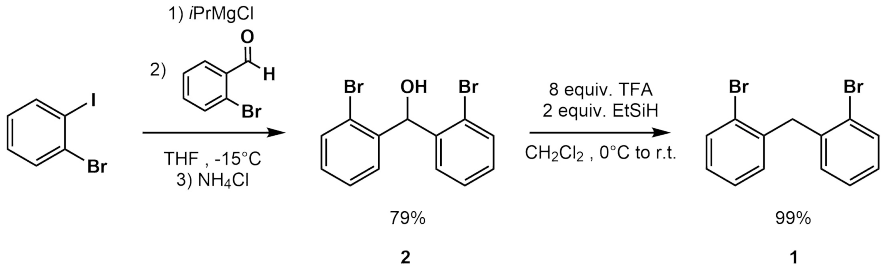


Scheme 2.6: Wang and co-workers synthesis of 4-styryl-diphenyl borane

Inspired by this new method of triarylboranes synthesis, we planned to extend this strategy to a general synthetic method of semi-cyclic triarylboranes. The synthesis of aminoethyldiphenyl borate, the synthesis of 4-styryl-diphenyl borate ammoniate and the removal of ammonia. At first sight we tried to apply this strategy to the synthesis 9-aryl-9,10-dihydro-9-boraanthracene.

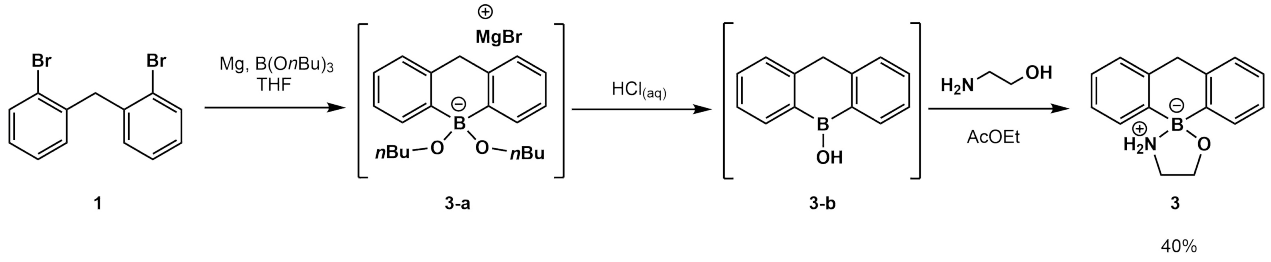
2.3 Synthesis of 9-aminoethyl-9,10-dihydro-9-boraanthracene

The starting material of our synthetic method being bis(2-bromophenyl)methane (**1**), this one is prepared using 1-iodo-2-bromobenzene and 2-bromobenzaldehyde according to Sparr and co-workers to form bis(2-bromophenyl)-methanol (**2**) which is then reduced (Scheme 2.7) [51].



Scheme 2.7: Synthesis of bis(2-bromophenyl)methane (**1**)

The barbier-type reaction of bis(2-bromophenyl)methane (**1**) with activated metallic magnesium in presence of $B(OR)_3$ as borylating agent affords, after treatment and addition of ethanolamine, the desired 2-aminoethoxy-9,10-dihydro-9-boraanthracene (**3**) with a yield of 40%.



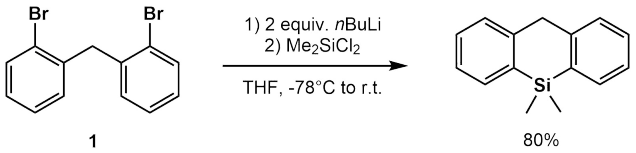
Scheme 2.8: Synthesis of 9-aminoethoxy-9,10-dihydro-9-boraanthracene (**3**)

A few optimisation steps were needed to improve the yield and understand which factors influence the yield of this reaction (Table 2.1).

Surprisingly, no desired product have been formed using a lithium source (Table 2.1 entry 1,2,3,4,5) and the ^{1}H NMR analysis always reveals a complex mixture. Different hypothesis could be cite to explain those results. First of all, with a pK_a value around 30, the benzydryl proton can be deprotonated in presence of *n*- or *t*butyl lithium which present pK_a values arroud 50. This hypothesis has been rapidly rejected due to the results reported by Feringa and co-workers who described the synthesis of 9-dimethyl-9,10-dihydro-9-silaanthracene from bis(2-bromophenyl)methane (**1**) using *n*butyl lithium with a yield of 80% (Scheme 2.9) [52].

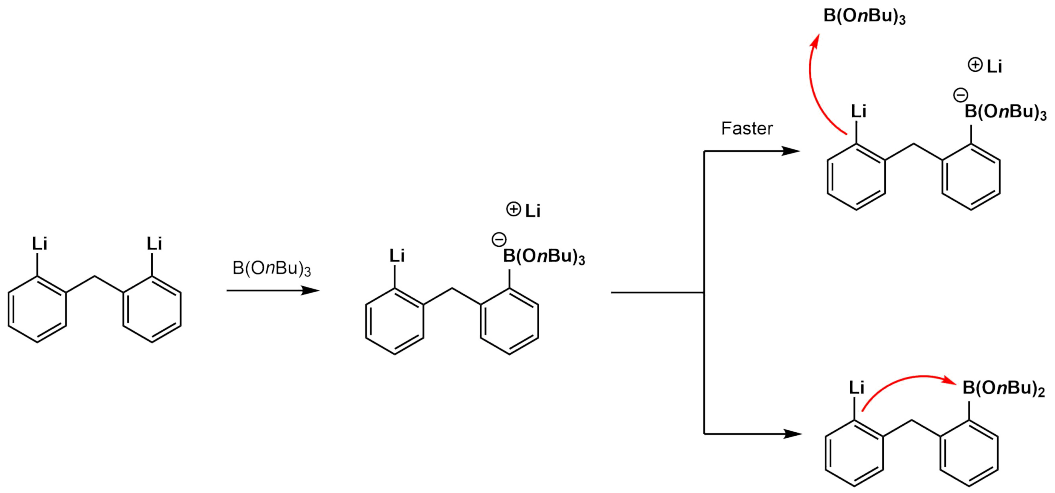
Table 2.1: Optimisation of the synthesis of 9-aminoethoxy-9,10-dihydro-9-boraanthracene (**3**)

	Metal source	Boron source	Amount of Mg or R−Li	Temperature	Reaction Time	Isolated yield
1	$nBuLi$	$B(OiPr)_3$	2 equiv.	−94 °C to r.t.	16 h	0%
2	$tBuLi$	$B(OiPr)_3$	4 equiv.	−94 °C to r.t.	16 h	0%
3	$tBuLi$	$B(OnBu)_3$	4 equiv.	−94 °C to r.t.	16 h	0%
4	$tBuLi$	$B(OMe)_3$	4 equiv.	−94 °C to r.t.	16 h	0%
5	$tBuLi$	$B(OnBu)_3$	4 equiv.	−94 °C to 40 °C	16 h	0%
6	Mg	$B(OiPr)_3$	3 equiv.	40 °C	16 h	54%
7	Mg	$B(OnBu)_3$	3 equiv.	40 °C	16 h	60%
8	Mg	$B(OnBu)_3$	3 equiv.	66 °C	72 h	17%
9	Mg	$B(OnBu)_3$	3 equiv.	20 °C	72 h	75%
10	Mg	$B(OnBu)_3$	3 equiv.	20 °C	3 h	53%



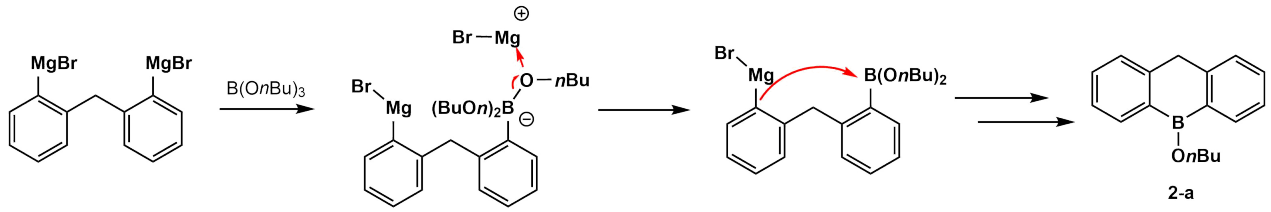
Scheme 2.9: Synthesis of 9-dimethyl-9,10-dihydro-9-silaanthracene reported by Feringa [52]

The major hypothesis to explain the difference of reactivity with lithium and magnesium is related to the mechanism of the reaction. After the addition of the lithium compound, a tetravalent boron is formed and then a decoordination of an alkoxy substituent is required to allow the intramolecullar second addition [53]. The addition of the organometallic species followed by a rapid decoordination is required to allow the final cyclisation step. In a presence of the dilithiated diphenylmethane, the slow rate of decoordination is in competition with the addition on a second trialkylborate (Scheme 2.10).



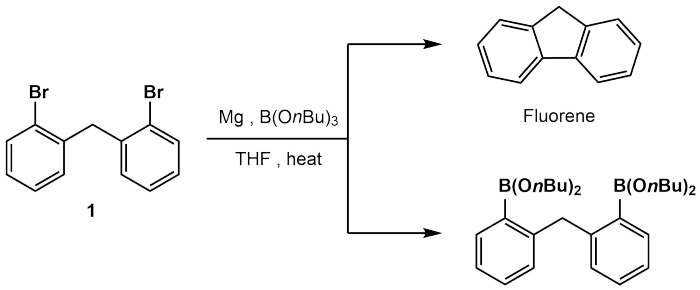
Scheme 2.10: Mechanism of lithiated bis(2-bromophenyl)methane in presence of $B(OnBu)_3$

In presence of an organomagnesium reagent, the decoordination of the alkoxy substituant is faster due to the higher oxophilicity of magnesium, compared to lithium, and allow the intramolecular reaction (Scheme 2.11) [54]. Furthermore, the reaction being performed in Barbier conditions, the Grignard formation is progressive which favour the intramolecular cyclisation (Scheme 2.11.



Scheme 2.11: Mechanism of decoordination of the *n*butoxy chain in presence of magnesium

Surprisingly, when the reaction was performed for 72h at reflux of THF, the yield decreased to 17% (Table 2.1 entry 8). Whereas a careful temperature control with a cold water bath resulted in a yield of 75% (Table 2.1 entry 9). When the temperature of the reaction is not carefully controled, different side reactions might occur but the major one is the formation of fluorene (Scheme 2.12).



Scheme 2.12: Putative side reaction during the formation of 9-diisopropoxy-9,10-dihydro-9-boraanthracene magnesium bromide (**3-a**)

Trimethyl, triisopropyl and tributyl borate do not display identical properties and stability. Addition of a Grignard reagent on triisopropyl borate is more difficult due to the steric hindrance of the isopropyl substituents. Considering trimethyl borate, this one is less stable and degrades itself easily in presence of water, forming borinic acid and methanol. Tributyl borate being reasonably stable and less hindered than triisopropyl borate constitutes the best boron source for this reaction (Figure 2.1) [55].

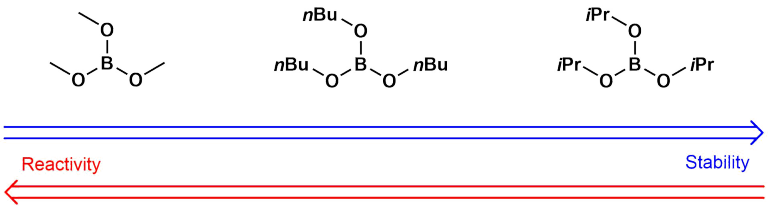
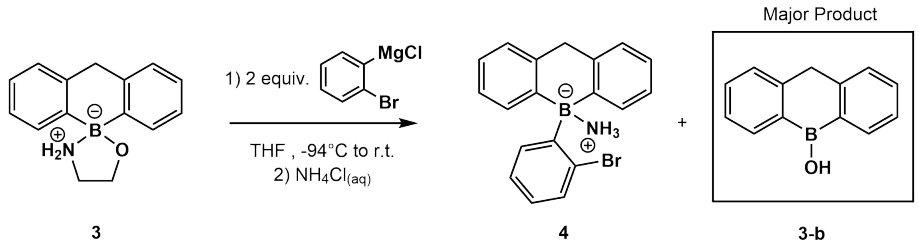


Figure 2.1: Stability and reactivity of different trialkyl borate

To conclude, 9-aminoethoxy-9,10-dihydro-9-boraanthracene (**3**) has been synthesized with 75% yield. This compound may be considered as an electrophile boron source, analogous to 9-chloro-9,10-dihydro-9-boraanthracene, but turns out to present an astonishing water and air stability compared to its analogous. Indeed, aminoethoxy boraantracene (**3**) may be poured into water without any degradation, or stored in open air for a long time before being used which present a significant interest.

2.4 Synthesis of 9-aryl-9,10-dihydro-9-boraanthracene ammoniate (3)

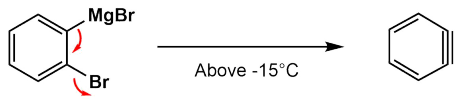
Since the synthesis of 9-aminoethoxy-9,10-dihydro-9-boratriptycene (**3**) has been optimized, the nucleophilic opening of 9-aminoethoxy-9,10-dihydro-9-boraanthracene (**3**) in presence of a grignard reagent has been preformed. The first reaction was carried out following the same procedure as described by Wang and co-workers, using two equivalents of 1-iodo-2-bromobenzene combined with isopropylmagnesium chloride, which is then added over a mixture of 9-aminoethoxy-9,10-dihydro-9-boraanthracene ammoniate (**3**) in THF [50]. The 9-(2-bromophenyl)-9,10-dihydro-9-boraanthracene (**4**) was obtained with a low yield, only 14% after aqueous ammonium chloride quench. Next, three equivalent of 2-bromophenyl Grignard were used, in those conditions the desired product was observed but the major product obtained was 9-hydroxy-9,10-dihydro-9-boraanthracene (**2-b**), which result from the acidic hydrolysis of 9-aminoethoxy-9,10-dihydro-9-boraanthracene (**3**). Those results show that the major part of 9-aminoethoxy-9,10-dihydro-9-boraanthracene (**3**) didn't react with the aryl Grignard and has simply been hydrolysed by the quench with saturated aqueous ammonium chloride (Scheme 2.13).



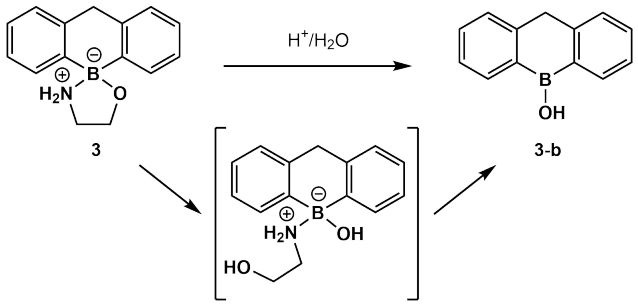
Scheme 2.13: Reaction of 2-bromophenyl Grignard with 9-aminoethoxy-9,10-dihydro-9-boraanthracene (**3**)

Actually, this result is due to the conditions in which the reaction is performed. The addition of the Grignard reagent over aminoethoxy boraanthracene (**3**) is performed at $-94\,^{\circ}\mathrm{C}$, the reaction is then allowed to warm at room temperature. The 2-bromophenyl Grignard is known to be unstable above $-15\,^{\circ}\mathrm{C}$ and allow the formation of benzyne before reacting with the aminoethoxy boraanthracene

(**3**) (Scheme 2.14). Consequently, all the remaining starting material is hydrolysed by the addition of aqueous ammonium chloride (Scheme 2.15).



Scheme 2.14: Mechanism of benzyne formation from 2-bromophenyl Grignard

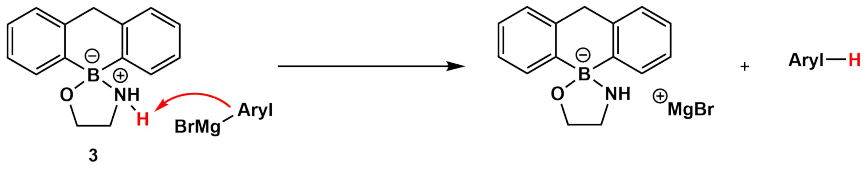


Scheme 2.15: Mechanism of 9-aminoethoxy-9,10-dihydro-9-boraanthracene (**3**) hydrolysis

The formation of borinic acid (**3-b**) is problematic due to the incompatibility of the 9-aryl-9,10-dihydro-9-boraanthracene ammoniate with silica gel chromatography. Therefore the best method to purify this compound turns out to be by precipitation in hexane. The hydrolysed and desired products being soluble in exactly the same solvent, it is absolutely necessary to avoid the formation of hydrolysed product (**3-b**).

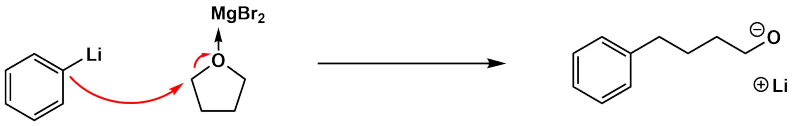
The reaction was then performed using phenyl magnesium bromide which is not susceptible to form benzyne. It remain intriguing why a poor yield was obtained using two equivalents of 2-bromophenyl magnesium bromide, while Wang and co-worker reported a yield of 74% using the same amount of Grignard reagent [50]. To answer this question, the reaction was performed using respectively one, two, three and four equivalents of phenyl phenyl magnesium bromide. With one equivalent, the only product observed was the 9-hydroxy-9,10-dihydro-9-boraanthracene (**3-b**), which correspond to the hydrolysed aminoethoxy boraanthracene (**3**). Using two equivalents, a mixture of desired and hydrolysed product was obtained with an ^{1}H NMR ratio of 40/60. The desired 9-phenyl-9,10-dihydro-9-boraanthracene ammoniate (**5**), was only obtained with satisfactory yields using three and four equivalents of Grignard reagent. The reason why fully hydrolysed product was observed with one equivalent is quite obvious. The aminoethoxy boraanthracene (**3**) carrying an acidic proton on the nitrogen atom, it is immediately deprotonated by the Grignard reagent (Scheme 2.16). The results obtained with two equivalent of Grignard reagent are much less obvious and no reasonable explanation have been identified so far. Surprisingly, a 43% yield was observed with three and four equivalents although no amminoethoxy boraanthracene (**3**) remained before aqueous ammonium chloride treatment. The ^{1}H and ^{11}B NMR

analysis of the filtrate reveals a complex mixture which doesn't provide any information. There's no reasonable explanations to this trend so far either.



Scheme 2.16: Deprotonation of 9-aminoethoxy-9,10-dihydro-9-boraanthracene (**3**) with aryl Grignard

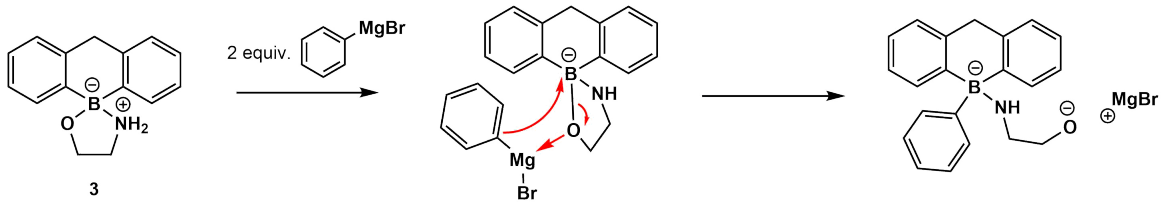
The reaction was subsequently attempted with three equivalents of phenyl lithium in exactly the same conditions as with phenyl magnesium bromide. The only product isolated was the borinic acid (**3-b**) with a low yield of 10%. Magnesium seems to have a key role in this reaction. In order to highlight the role of magnesium, the reaction was performed using three equivalents of phenyl lithium solution added over aminoethoxy boraanthracene (**3**) in presence of three equivalents of magnesium bromide. The hydrolysed product was obtained with 90% yield and the ^{1}H and ^{11}B NMR analysis of the filtrate reveals the formation of 4-phenyl-1-butanol which is the product of addition of phenyl lithium over THF (Scheme 2.17). This result suggests a Lewis acidic activation of THF by the magnesium bromide which allows the nucleophilic addition of phenyl lithium over THF.



Scheme 2.17: Probable reaction of phenyl lithium with THF in presence of magnesium bromide

The addition of magnesium bromide had absolutely no impact on the addition of phenyl lithium over aminoethoxy boraanthracene (**3**). However the most reasonable hypothesis to explain this difference of reactivity of phenyl lithium and Grignard towards aminoethoxy boraanthracene (**3**) is the highly basic character of phenyl lithium. The phenyl lithium might deprotonate the benzhydril proton and the amino group which may involve some uncontrolled side reactions. Concerning the reactivity of phenyl magnesium, the most reasonable hypothesis implies the chelating ability of the magnesium which may favour the opening of the ethanolamine ring on the oxygen side, while the nucleophilic carbon attacks on the boron atom (Scheme 2.18). Moreover, in addition of its chelating ability, magnesium presents an oxophilicity twice higher than lithium which may be a point in favour of the proposed mechanism [54].

We then employed various aryl Grignard reagents to synthesize several 9-aryl-9,10-dihydro-9-boraanthracene with mono *ortho*- and *meta*- substituents on the phenyl ring. Those compounds were obtained with moderate yields of 40-50% (Figure 2.2).



Scheme 2.18: Proposed mechanism of ethanolamine ring opening in presence of phenyl magnesium

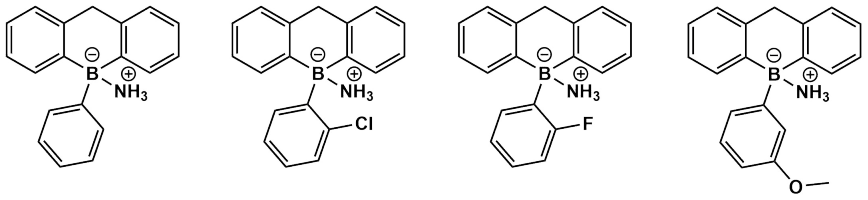


Figure 2.2: 9-aryl-9,10-dihydro-9-boraantracene with mono *ortho*- or *meta*-substituted phenyl ring

More functionalized aryl Grignard reagents were subsequently synthesized and the presence of two *ortho*-substituents such as fluorine was tolerated (Figure 2.3). Addition of hindered or strongly electron depleted phenyl rings is often difficult due to a decrease of reactivity but provided in our case the desired borane ammoniates with yields of 21-48%. Furthermore, the addition of strongly electron depleted aromatic rings on a boron atom will increase the Lewis acidity of the resulting compound.

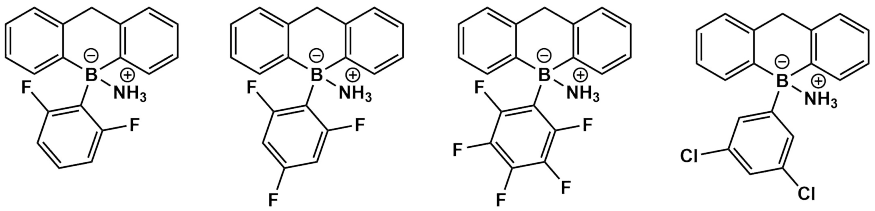
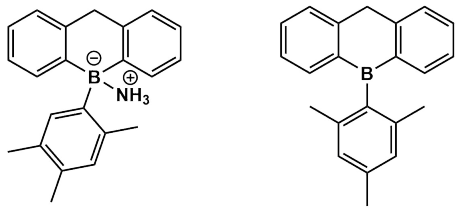


Figure 2.3: 9-aryl-9,10-dihydro-9-boraantracene with poly substituted phenyl ring

Two other 9-aryl-9,10-dihydro-9-boraanthracene have been synthesized with different methyl substituents on different positions of the phenyl ring. Those compounds will probably not present a strong Lewis acidity on the boron atom due to the inductive electron donor character of the methyl groups but the steric hindrance of the methyl group may show interesting properties in the context of frustrated Lewis pairs (Figure 2.4).

The results obtained concerning 9-mesityl-9,10-dihydro-9-boraanthracene (**14**) present some particular features. Indeed this compound has been directly isolated in the borane form and not as the ammonia adduct due to the very bulky mesityl substituent. Interestingly, in presence of mesityl magnesium bromide different products are formed (Scheme 2.19). The dimer (**15**) has been unambiguously

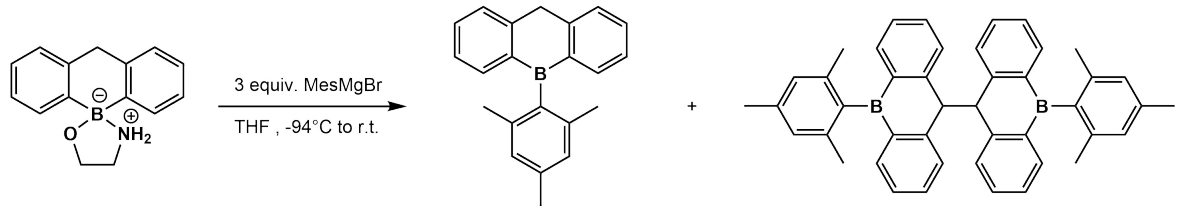


13 **14**

27% 26%

Figure 2.4: 9-aryl-9,10-dihydro-9-boraantracene with methyl substituants on the phenyl ring

characterized by NMR and X-ray analysis and its formation is surprising considering the absence of formation of that kind of product in all the other cases. The dimerisation of **14** is not spontaneous which has been proved by dissolving it in THF and leaving for several days in open air without noticing any dimerisation.



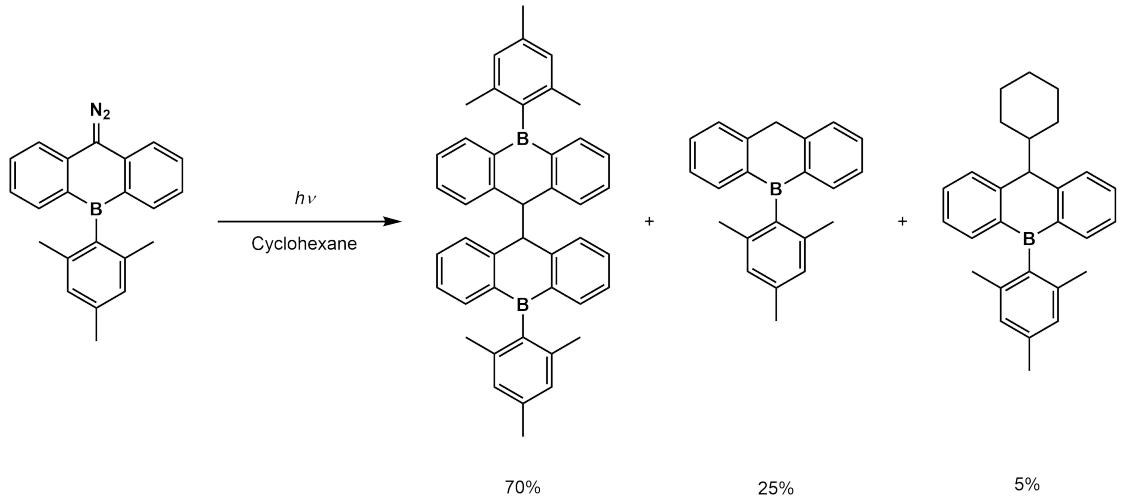
3 **14** **15**

21% 15%

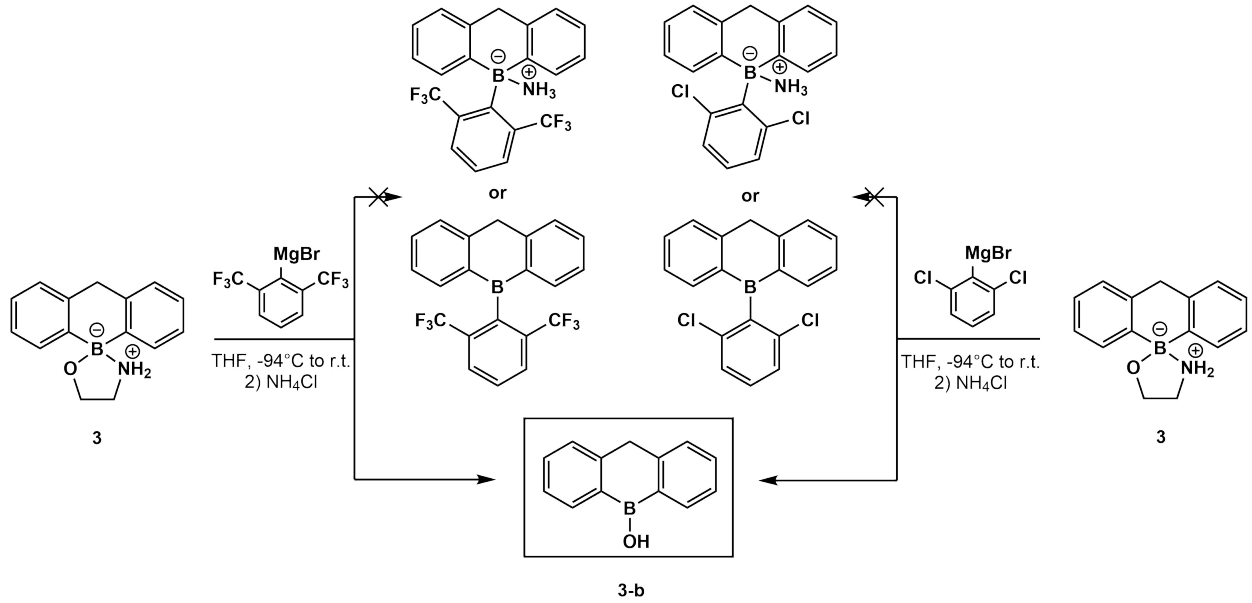
Scheme 2.19: Reaction of 9-aminoethoxy-9,10-dihydro-9-boraanthracene (**3**) with mesityl Grignard

This compound is described in the literature but the synthesis presented is completely different. The synthesis of this compound involve the preliminary formation of diazoboraanthracene which is irradiated and partially forms the dimer compound, which means that 9-mesityl-9,10-dihydro-9-boraanthracene (**14**) has to be previously synthesized (Scheme 2.20) [56]. The mesityl boraanthracene (**14**) is synthesized using Jutzi or Bickelhaupt method which have been previously described [47], [48]. The mesityl boraanthracene seems to present interesting oxido-reduction properties which may, combined with the light present in the lab during the reaction, allow the formation of the dimer. The mechanism of this reaction being far from the subject of our study, it as not been studied in more details.

Our methodology displays several limitations, in fact no reactivity was observed when bulkier phenyl rings than mesityl are used such as $-\mathrm{Cl}$ and $-\mathrm{CF_3}$ substituents in *ortho*-position (Scheme 2.21). The absence of reactivity with two chloro-substituents in *ortho*-position is surprising, 2,6-dichlorophenyl being less hindered than mesityl. In this case the absence of reaction may be attributed to lower reactivity of 2,6-dichlorophenyl added to the steric hindrance.



Scheme 2.20: Known synthesis of 9-mesityl-9,10-dihydro-9-boraanthracene dimer [56]



Scheme 2.21: Reaction of 2,6-bis(trifluoromethyl)phenyl Grignard and 2,6-dichlorophenyl Grignard with 9-aminoethoxy-9,10-dihydro-9-boraanthracene (**3**)

The absence of reactivity observed using phenyl magnesium bromide with bulky *ortho*-substituents may be explained by the X-ray structure of 9-aminoethoxy-9,10-dihydro-9-boraanthracene (**3**). This reveals that the anthracene structure is not planar as it could be expected but reveals a bending of $37.16°$. The cycle formed by ethanolamine is nearly perpendicular with the anthracene structure. It is important to note that the B-O bond is about $(1{,}467 \pm 0{,}003)$ Å which is shorter than a standard B-O bond ($1{,}53$ Å). Furthermore the oxygen atom is located in concave side of the anthracene ring. Following the postulated mechanism, the grignard reagent would add on the boron atom by the oxygen side. This side of the molecule is the most hindered consequently the addition of a bulky Grignard reagent would turn out to be difficult (Figure 2.5 and Table 2.2).

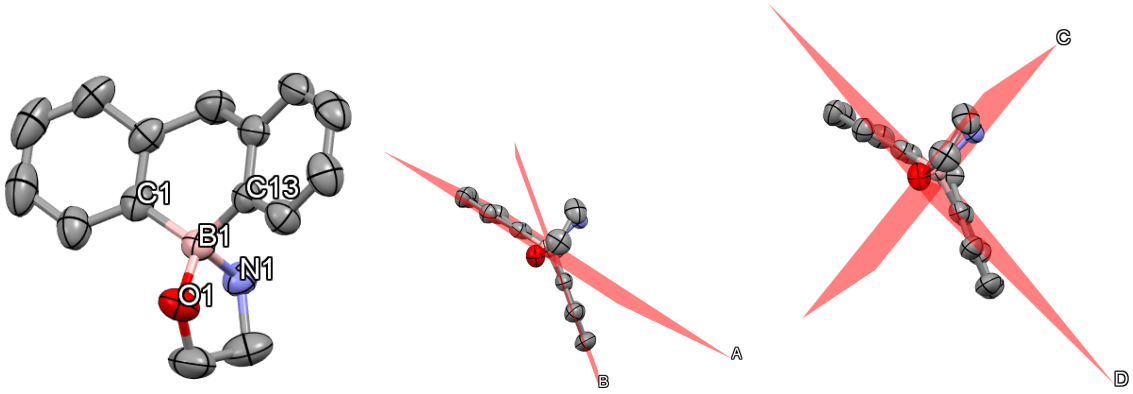


Figure 2.5: X-ray structure of 9-aminoethoxy-9,10-dihydro-9-boraanthracene (**3**)

Table 2.2: Relevant bond length and angle values of 9-aminoethoxy-9,10-dihydro-9-boraanthracene (**3**)

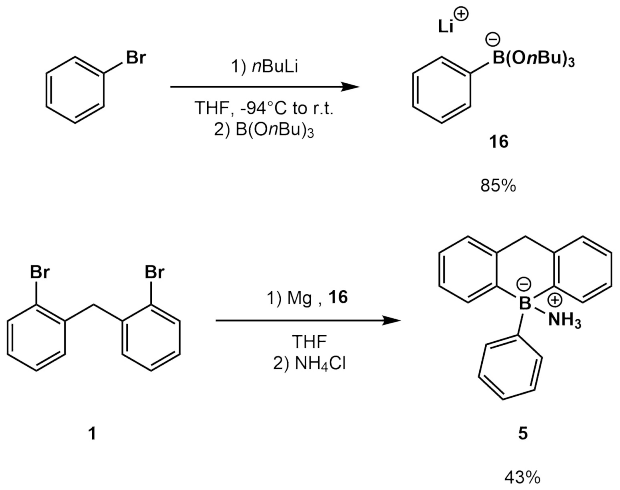
Atoms	Bond length Å	Atoms	Bond angle °
B(1)-**O**(1)	1.478(3)	**O**(1)-**B**(1)-**N**(1)	100.6(2)
B(1)-**N**(1)	1.656(3)	**O**(1)-**B**(1)-**C**(1)	113.1(2)
B(1)-**C**(1)	1.603(3)	**N**(1)-**B**(1)-**C**(1)	109.9(2)
B(1)-**C**(13)	1.608(3)	**O**(1)-**B**(1)-**C**(13)	113.5(2)
C(7)-**C**(6)	1.505(4)	**N**(1)-**B**(1)-**C**(13)	108.9(2)
B(7)-**O**(8)	1.510(4)	**C**(1)-**B**(1)-**C**(13)	110.3(2)
		C(6)-**C**(7)-**C**(8)	114.7(2)
		(**A**-**B**)plan	37.16
		(**C**-**D**)plan	87.41

To summarize, aminoethoxy boraanthracene (**3**) displays some drawbacks : three equivalents of aryl magnesium bromide are required to obtain the best yields, two steps are required from bis(2-bromophenyl)methane (**1**) to 9-aryl-9,10-dihydro-9-boraanthracene ammoniate and none of these steps are quantitative.

2.5 One-pot synthesis of 9-aryl-9,10-dihydro -9-boraanthracene ammoniate

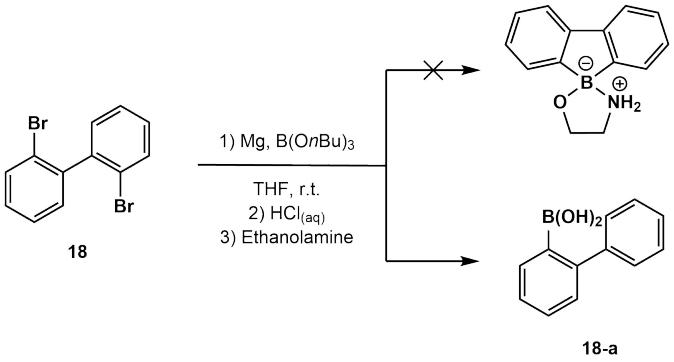
In order to overcome those issues, a semi-one pot reaction was performed. First, lithium phenyl tributylborate is synthesized using phenyl lithium which is quenched using tributylborate. This compound is then mixed with bis(2-bromophenyl)methane (**1**) in THF and this mixture is added slowly over preactivated metallic magnesium (Scheme 2.22).

Surprisingly, in these conditions, 9-phenyl-9,10-dihydro-9-boraanthracene ammoniate (**5**) has been isolated with 43% yield. Furtermore the synthesis of the lithium phenyl tributylborate (**16**) is quantitative and air stable enough to be easily purified via recristallisation in open air. Considering

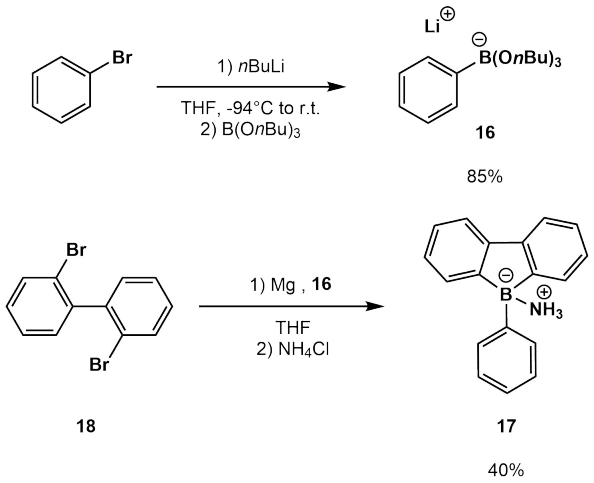


Scheme 2.22: Semi one-pot synthesis of 9-phenyl-9,10-dihydro-9-boraanthracene ammoniate (**5**)

those results, the synthesis of 9-phenyl-9-borafluorene ammoniate (**17**) has been attempted using this methodology. Indeed, this compound present some interesting and strong Lewis acidic properties and has only been synthesized using Jutzi method. The complex synthesis and the Lewis acidic properties of this compound are due to its anti-aromatic character. The synthesis of the corresponding borinic acid is also impossible due to its rapid degradation which prevents the synthesis of the aminoethoxy borafluorene. The synthesis of that kind of compound via a more straightforward pathway would be of real interest. The formation of the 9-hydroxy-9-borafluorene being impossible, the formation of the complex with ethanolamine is also impossible and our first method failed, the only product formed was the product of protodeborylation, namely 2-biphenyl boronic acid (**18-a**) (Scheme 2.23). Against all odds, the reaction using bis(2-bromo)biphenyl (**18**) and phenyl tributylborate (**16**) succeed and the 9-phenyl-9-borafluorene ammoniate (**17**) was synthesized with 40% yield (Scheme 2.24).

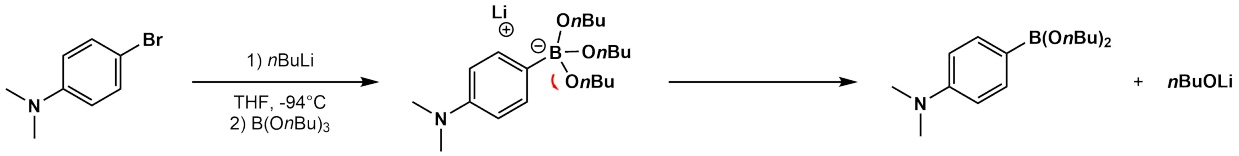


Scheme 2.23: Attempted synthesis of 9-amonoethoxy-9-borafluorene



Scheme 2.24: Semi one-pot synthesis of 9-phenyl-9-borafluorene ammoniate (**17**)

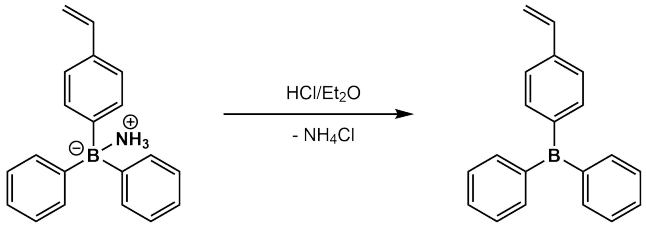
Considering those encouraging results, different lithium aryl tributylborate have been synthesized such as lithium pentafluorophenyl tributylborate or lithium pentachlorophenyl tributylborate. Those compound have been synthesized with the same yields as lithium phenyl tributylborate (**16**) but the major limitation of this method emerged. Those aryl tributylborate are quite insoluble in THF or diethyl ether which makes impossible to mix those compound with bis(2-bromophenyl)methane (**1**) or bis(2-bromo)diphenyl (**18**) and THF in a dropping funnel. To overcome the solubility issues, it is eventually possible to synthesize aryl dibutylborinate but those compounds are much less air stable and have to be purified via distillation which become much less straightforward than the methodology using ethanolamine. Furthermore, the synthesis of aryl tributylborate using electron-rich or strong electron donating aryl substituent, such as dimethylaniline, turns out to be difficult due to the limited stability of the corresponding aryl tributylborate (Scheme 2.25).



Scheme 2.25: Degradation of 4-dimethylaniline-tributylborate into 4-dimethylaniline-dibutylborinate

2.6 Deprotection of 9-aryl-9,10-dihydro-9-boraanthracene ammoniate : Removal of ammonia

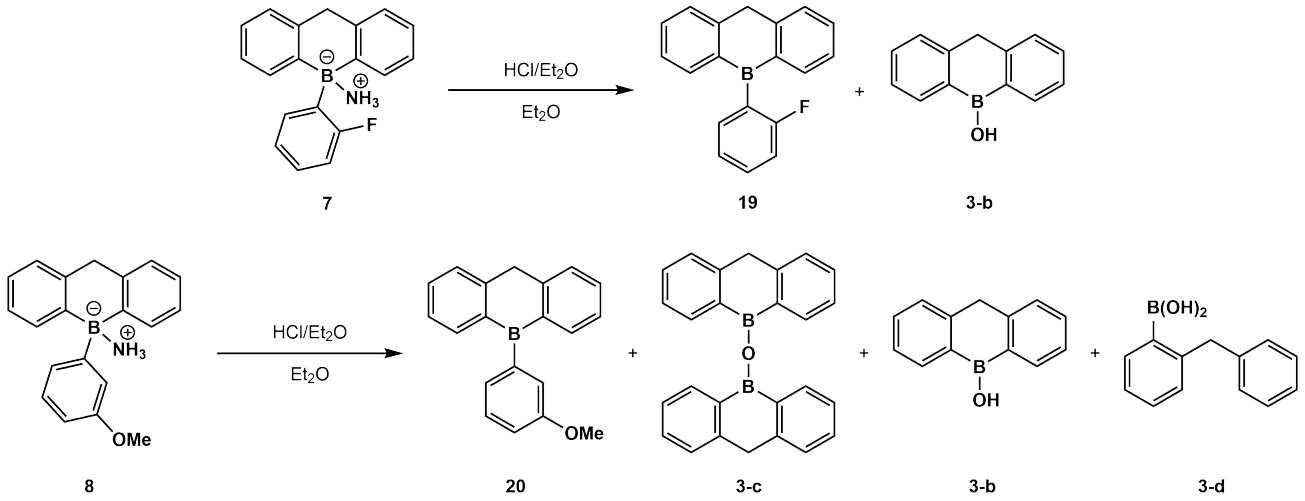
Having in hands several *N*-protected 9-aryl-9,10-dihydro-9-boraanthracene ammoniates the deprotection of the boron atom and removal of ammonia constitutes the last step of the synthesis of semi-cyclic triarylboranes. Wang and co-workers described the removal of ammonia for their 4-styryl-diphenylborane ammoniate using a solution of hydrochloric acid in diethylether (Scheme 2.26) [50].



Scheme 2.26: Deprotection of 4-styryl-diphenylborane ammoniate using HCl in Et_2O described by Wang and co-workers

The hydrochloric acid protonates ammonia which precipitate in the form of solid ammonium chloride. The use of hydrochloric acid in an anhydrous solvent is important to avoid the formation of byproduct formed by protodeborylation. However, Wang and co-workers described the formation of byproduct and their desired product was purified by repeated recristallisation in diethylether. The same procedure was applied to our 9-(2-fluorophenyl)-9,10-dihydro-9-boraanthracene ammoniate (**7**) but we were not able to obtain the desired product via recristallisation. The ^1H NMR reveals a complex mixture while the ^{11}B NMR reveals the presence of the desired product (**21**) and 9-hydroxy-9,10-dihydro-9-boraanthracene (**3-b**) (Scheme 2.27 and Figure Figure 2.6). The reaction was also carried out with 9-(3-methoxyphenyl)-9,10-dihydro-9-boraanthracene amoniate (**8**) and in this case the ^{11}B analysis of the mixture, revealed the presence of desired product, borinic acid derivative (**3-b**), borinic anhydride (**3-c**) and boronic acid derivative (**3-d**) (Scheme 2.27).

With solutions of HCl in dioxane and HBF_4 in Et_2O, even with a fresh solution of HBF_4 in Et_2O, the crude mixture contained a lot of impurities. Given the fact that a purification by precipitation turned out to be very difficult, a sublimation of the crude was carried out but did not succeed. Consequently, we preferred to use another deprotection method. The following deprotection tests have been preformed in a glovebox using various Lewis acids and strong electrophiles to displace the ammonia. In a first instance, $BF_3 \cdot Et_2O$ was mixed with 9-phenyl-9-borafluorene ammoniate (**17**) in CD_2Cl_2 and the ^{11}B NMR was immediately recorded (Scheme 2.28). The results only show the presence of the deprotected form of 9-phenyl-9-borafluorene (**21**) but due to the intensity of the signal corresponding to $BF_3 \cdot Et_2O$, the presence of another signal from 5 ppm to -5 ppm would be difficult to distinguish, consequently



Scheme 2.27: Deprotection of 9-(2-fluorophenyl)-9,10-dihydro-9-boraanthracene ammoniate (**7**) and 9-(3-anisole)-9,10-dihydro-9-boraanthracene ammoniate (**8**) using solution of HCl in Et_2O

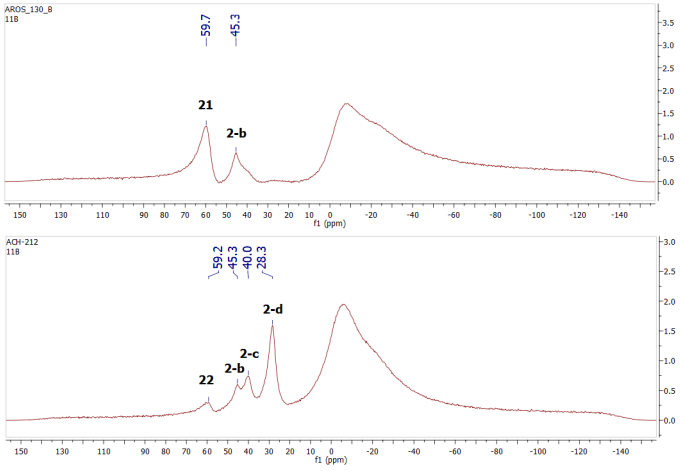
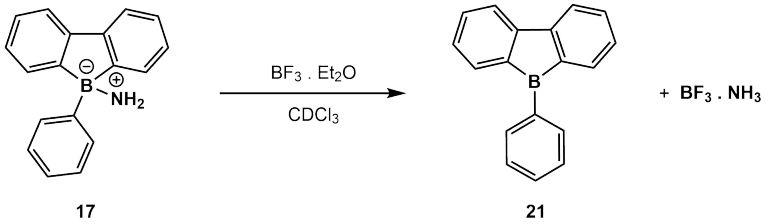


Figure 2.6: ^{11} NMR of 9-(2-fluorophenyl)-9,10-dihydro-9-boraanthracene ammoniate (**7**) (above) and 9-(3-anisole)-9,10-dihydro-9-boraanthracene ammoniate (**8**) (below) deprotection reaction crude product using solution of HCl in Et_2O.

the signal of $BF_3 \cdot NH_3$ normally appearing at -0.2 ppm was impossible to distinguish (Figure 2.7). This method seems to be quite efficient but not practical due to the remaining $BF_3 \cdot Et_2O$ which turns out to be difficult to remove.



Scheme 2.28: Deprotection of 9-phenyl-9-borafluorene ammoniate (**17**) using $BF_3 \cdot Et_2O$

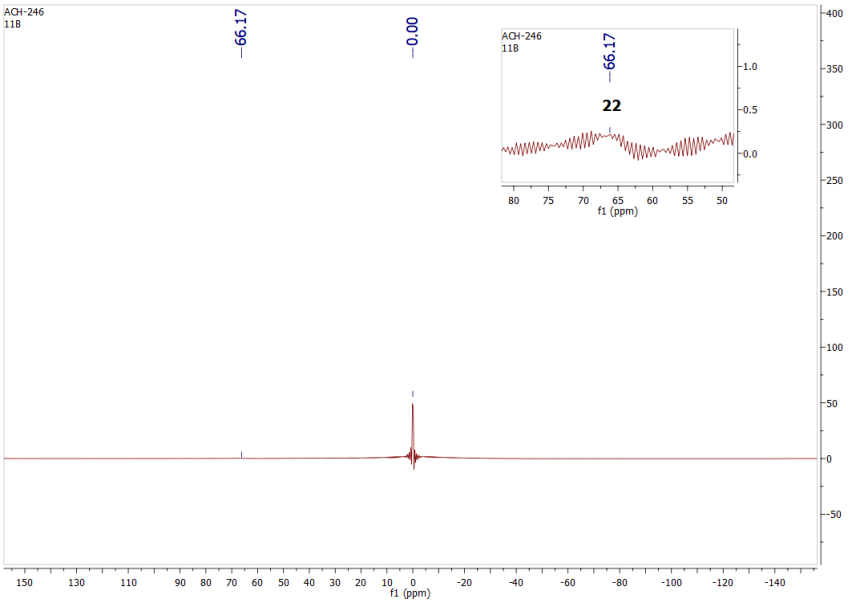


Figure 2.7: ^{11}B NMR sepctrum of the crude reaction product of 9-phenyl-9-borafluorene ammoniate (**17**) using $BF_3 \cdot Et_2O$

We envisioned that a strong methylating agent would methylate ammonia and release the borane and the methylammonium salt. The first attempted reaction was performed with 9-(2,4,6-trifluorophenyl)-9,10-dihydro-9-boraanthracene ammoniate (**10**) and three equivalents of iodomethane. According to the ^{11}B NMR analysis, iodomethane might not be a sufficiently strong methylating agent. We replaced it with trimethyloxonium tetrafluoroborate, also known as Meerwein salt, which is one of the strongest methylating agent. The reaction was first performed in chloroform and analysed by ^{11}B NMR which reveals the presence of the deprotected borane (**22**) (^{11}B NMR : 59.5 ppm, ^{19}F NMR : 97.8 and 108.7 ppm) as well as the starting material (**10**) (^{11}B NMR : 8.3 ppm, ^{19}F NMR : 100.9 and 113.4 ppm) but, most importantly, no degradation product have been detected (Figure 2.8).

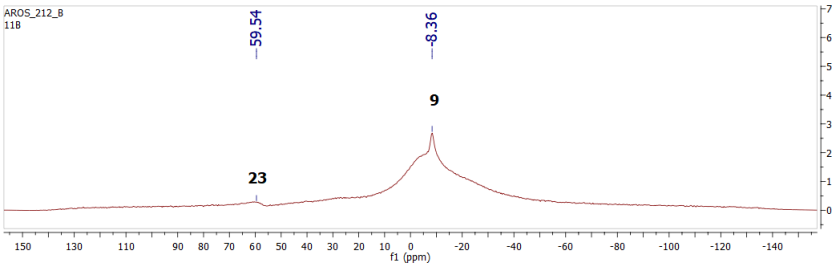


Figure 2.8: ^{11}B NMR spectrum of the crude reaction product of 9-(2,4,6-trifluorophenyl-9,10-dihydro-9-boraanthracene ammoniate (**10**) using one equivalent of Meerwein salt in $CDCl_3$

Following those preliminary observations, the reaction was performed using 10 equivalents of Meerwein salt. The results show that the amount of desired product (**22**) increased and the amount of starting material (**10**) decreased (Figure 2.9), according to the ^{19}F NMR only 14% of the starting

material (**10**) remained. The remaining presence of starting material (**10**) might be explained by the low solubility of Meerwein salt in chloroform mixed with the difficulties to stir efficiently the mixture in the glove box.

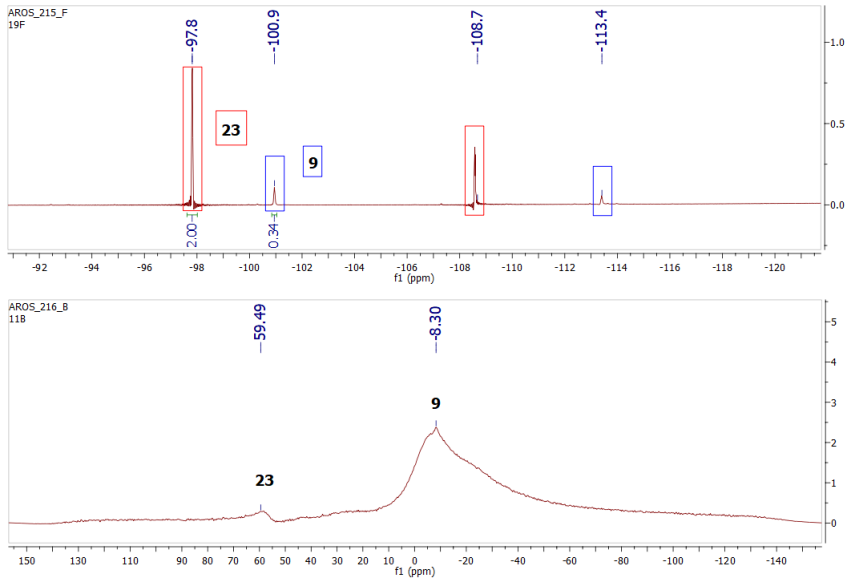
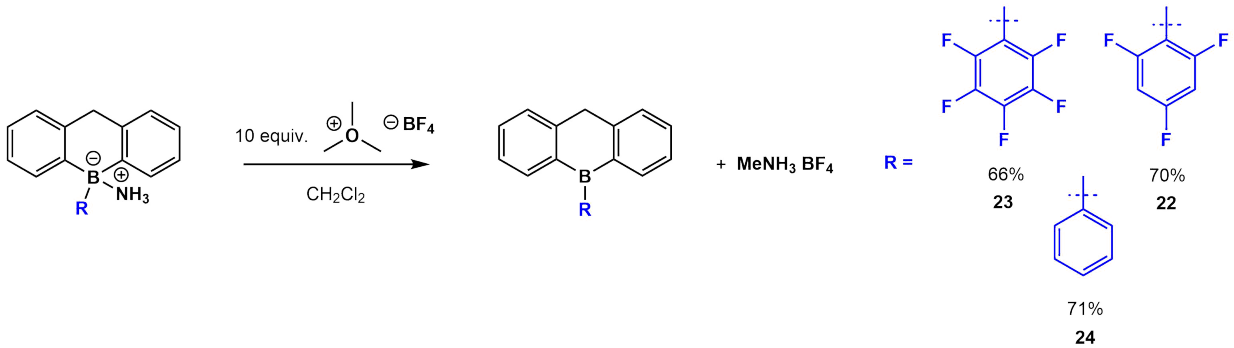


Figure 2.9: ^{19}F NMR (above) and ^{11}B NMR (below) spectra of the crude reaction product of 9-(2,4,6-trifluorophenyl-9,10-dihydro-9-boraanthracene ammoniate (**10**) using 10 equivalent of Meerwein salt in $CDCl_3$

Accordingly, the same reaction was performed using 10 equivalent of Meerwein salt in methylene chloride as solvent. Visualy, the aspect of the reaction was a bit different. In chloroform, Meerwein salt formed a lot of little aggregates were observed while in methylene chloride, Meerwein salt was also quite insoluble but formed an homogeneous dispersion. According to ^{11}B NMR analysis, the deprotected borane (**22**) was quantitatively formed with full conversion (Figure 2.10).

This reaction was performed with several 9-aryl-9,10-dihydro-9-boraanthracene ammoniate and the yields are ranging between 65 and 75% which is due to the purification steps in order to remove all traces of Meerwein salt (Scheme 2.29).



Scheme 2.29: Deprotection of 9-aryl-9,10-dihydro-9-boraanthracene ammoniate using Meerwein salt

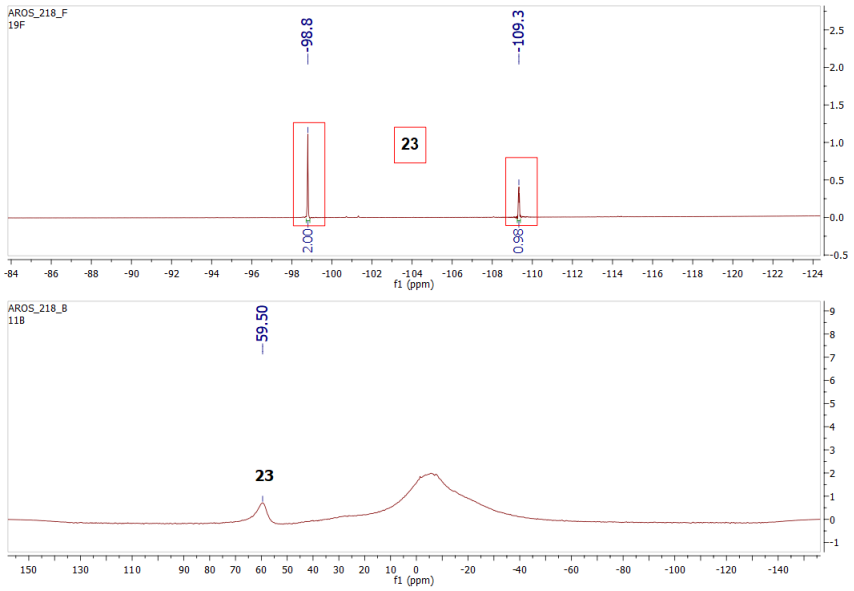


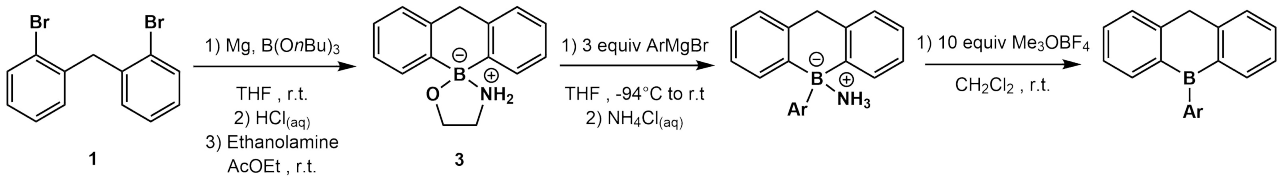
Figure 2.10: ^{19}F NMR (above) and ^{11}B NMR (below) spectra of the crude reaction product of 9-(2,4,6-trifluorophenyl-9,10-dihydro-9-boraanthracene ammoniate (**10**) using 10 equivalent of Meerwein salt in CD_2Cl_2

2.7 Conclusion and perspectives

Semi-cyclic triaryl borane are poorly studied in the literature. The synthesis of such compounds remain problematic and involve the use of highly toxic or sensitive compounds which have to be generally stored in glovebox. In the context of frustrated Lewis pair where tris(pentafluorophenyl)borane is the most commonly used Lewis acid, it appeared important to synthesize and study the Lewis acidic properties of those semi-cyclic triaryl boranes. Furthermore, considering the increasing attention devoted to air and moisture stable boron Lewis acids, the particular structure of this type of boranes may present some advantages. In this context, the objective of this work was clear : provide a reproducible and straightforward synthesis of 9-aryl-9,10-dihydro-9-boraanthracene, study their Lewis acidic properties and their air and moisture stability compared to classical triarylboranes.

Several 9-aryl-9,10-dihydro-9-boraanthracene were synthesized in a three step synthesis starting from bis(2-bromophenyl)methane which does not require the use of highly toxic or sensitive reagents (Scheme **??**). The 9-aminoethoxy-9,10-dihydro-9-boraanthracene (**3**) used as precursor of 9-aryl-9,10-dihydro-9-boraanthracene turns out to be an highly stable synthetic equivalent to the highly moisture sensitive 9-chloro-9,10-dihydro-9-boraanthracene. Several aryl and *ortho*-substituted aryl substituents have been attached to the 9,10-dihydro-9-boraanthracene scaffold which present significant electron attracting properties in order to increase the Lewis acidity of the boron atom.

The Lewis acidic properties and the stability towards moisture are yet to be tested. Considering



Scheme 2.30: Synthesis of 9-aryl-9,10-dihydro-9-boraanthracene

the high sensitivity of the corresponding triphenylborane, the stability of 9-aryl-9,10-dihydro-9-boraanthracene represent an important point for further applications. Indeed, considering the increasing demand for aryl boranes different from BCF and more stable than triphenyl borane, these new semi-cyclic aryl boranes may find applications in organic catalysis. Furthermore, the particular semi-cyclic structure with an anthracene scaffold may easily be tuned with several substituents and then confer to those 9-aryl-9,10-dihydro-9-boraanthracene infinite properties.

CHAPTER 3

Synthesis of 9-boratriptycene

3.1 Introduction

In 1989, Massey described the 9-boratriptycene as an interesting molecule which may present particular Lewis acidic properties [57]. Those assumptions derived only from the particular structure of this compound. Indeed, the 9-boratriptycene is a tridimensional triptycene structure in which a boron atom is incorporated in the bridgehead position. This compound remained strictly hypothetical and was forgotten from the literature until Timoshkin studied it in 2011 by theoretical calculations and compared it with different boron Lewis acids and their aluminium and gallium equivalents. The dissociation energy between the Lewis acids and ammonia has been studied which represents a quantitative way to evaluate and compare the Lewis acidity. The higher the dissociation energy is, the stronger the Lewis acid is. This theoretical study highlighted the Lewis acidic potential of the 9-boratriptycene which is predicted to be one of the strongest neutral boron Lewis acid known (Figure 3.1) [9].

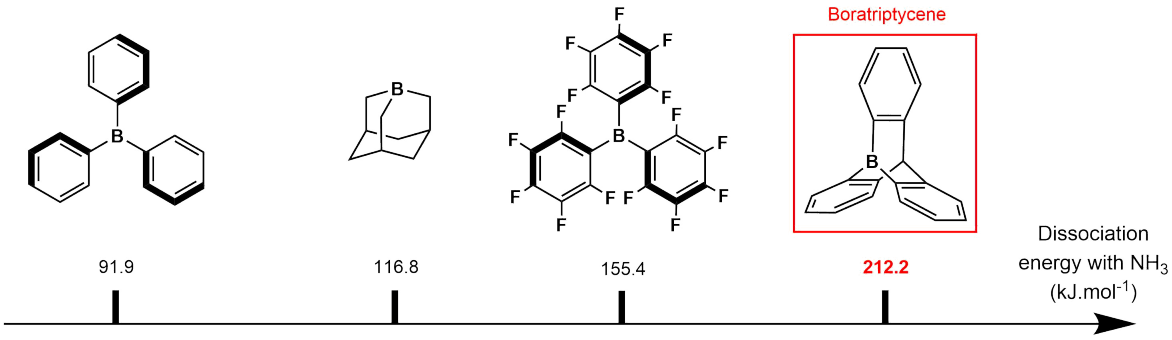


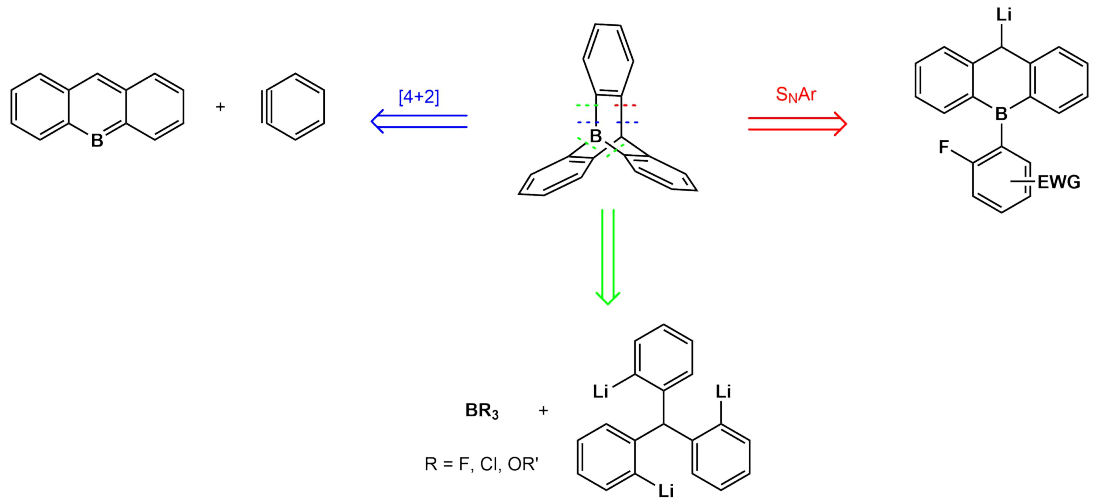
Figure 3.1: Dissociation energy with ammonia of different boron Lewis acids.

The 9-boratriptycene has a dissociation energy with ammonia of $212\,\mathrm{kJ\,mol^{-1}}$, around $60\,\mathrm{kJ\,mol^{-1}}$ higher than trispentafluorophenyl borane (BCF), which is one of the most employed, stable and nearly one of the strongest Lewis acid to date. The difference concerning the energy dissociation with

ammonia between BCF and triphenyl borane is also around $60\,\mathrm{kJ\,mol^{-1}}$ [9]. Triphenyl borane being a quite weak Lewis acid and BCF nearly one of the strongest, it illustrates the predicted unprecedented Lewis acidity of 9-boratriptycene.

3.2 Synthesis of boratriptycene

Regarding the predicted Lewis acidic properties of the 9-boratritpycene, the objective of this work is quite simple : provide a reproducible synthesis of the trivalent 9-boratriptycene. The boratriptycene subject being approached in only two publications and all of them being theoretical approach, the field of the synthesis is completely unexplored and there is no obvious starting point [9] [57]. Our starting point to find different pathway to synthesize this new molecule was performing a retro-synthetic analysis (Scheme 3.1).



Scheme 3.1: Proposed retrosynthesis of 9-boratriptycene.

Keeping in mind the predicted very high Lewis acidity of this compound, we preferred to protect the boron atom under its tetracoordinated form by using a group that might be removed once the desired product will be synthesized and purified. The use of a protecting group will avoid side reactions during the synthesis and may also facilitate the synthesis of the molecule from a thermodynamic point of view. Indeed, as discussed before, the pyramidalisation of the boron atom in the 9-boratriptycene structure is not natural. If the reaction to form the 9-boratriptycene is performed using a trivalent boron atom, the required energy barrier to perform the cyclisation reaction might be too high from a thermodynamic point of view. However, using a tetravalent boron atom to perform threefold borylative cyclisation would be much more easy due to the initial tetrahedral form of the boron atom. In this case the distortion on the boron atom will be nearly identical in the reagents and products and the

cyclisation should therefore be easier, except in the case of 9-boraanthracene in which the tetravalent boron remains planar (Figure 3.2).

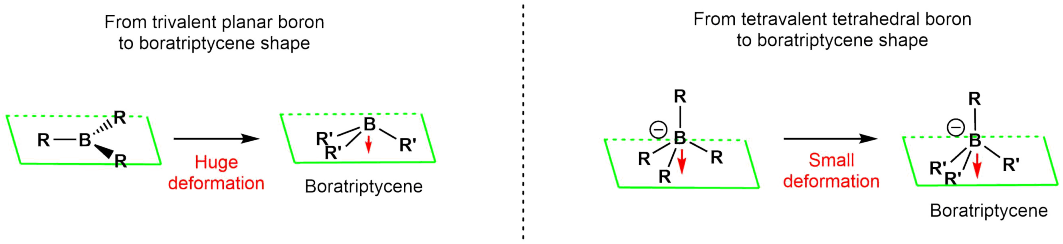
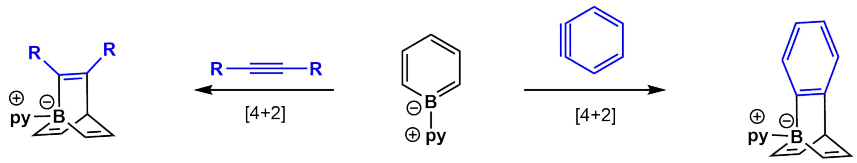


Figure 3.2: Deformation induced by the formation of the boratriptycene shape in the case of trivalent pyramidal and tetravalent tetrahedral boron atom.

We focused on the three strategies described above to form the 9-boratriptycene. In 2006, the first synthesis of borabarrelene and borabenzobarrelene via Diels-Alder addition to borabenzene was reported by Piers and co-workers (Scheme 3.2) [35]. The 9-boraanthracene being a suitable precursor and already known in the litterature, it is thus logical to start our synthetic investigations at this point [58].

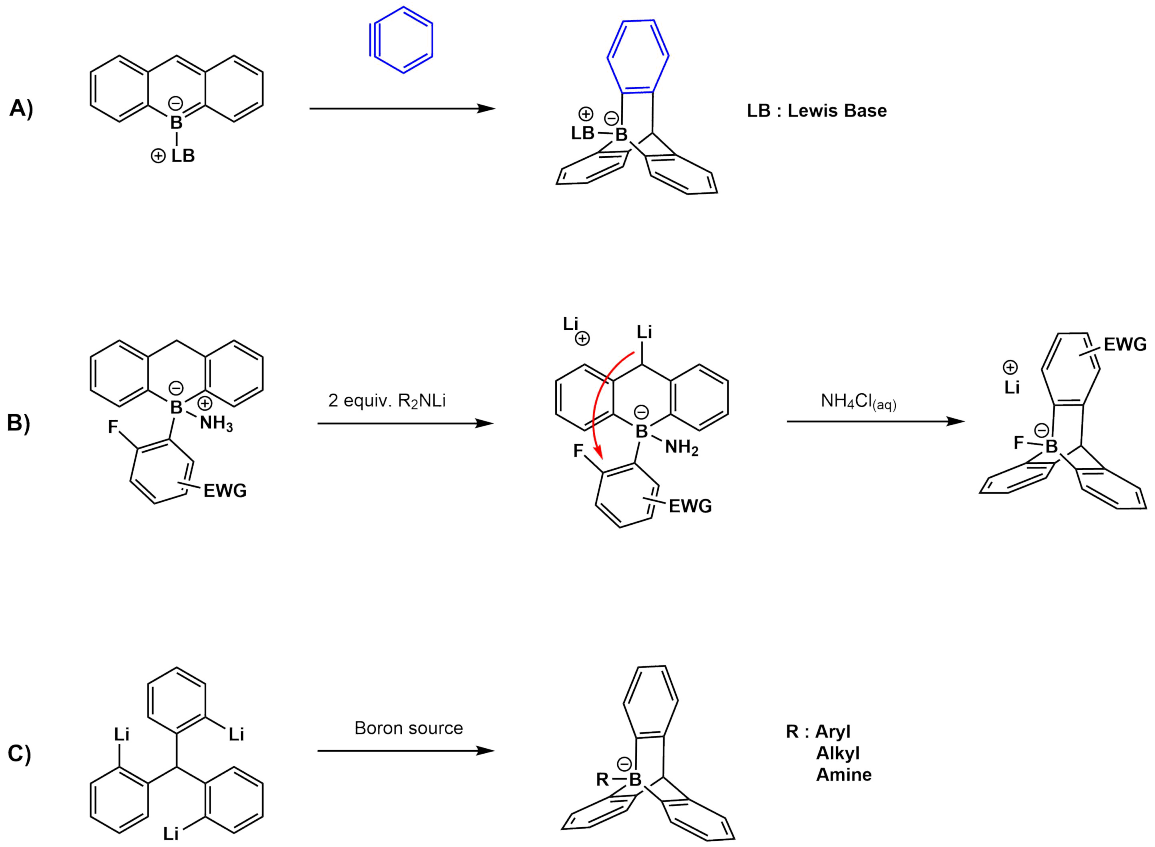


Scheme 3.2: Synthesis of borabarrelene and benzoborabarrelene via Diels-alder addition to borabenzene.

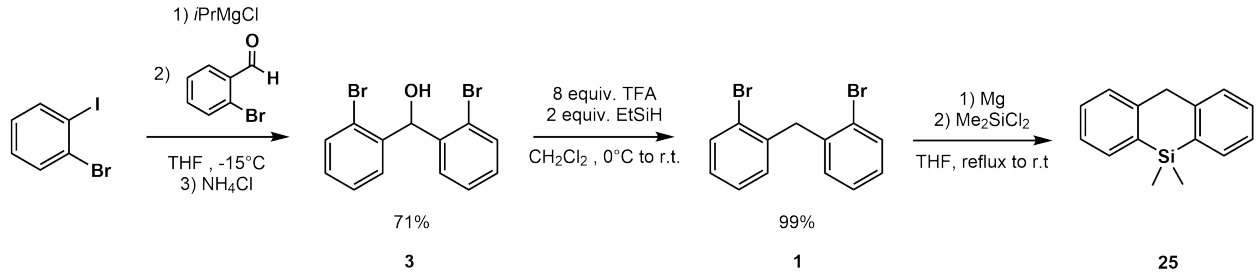
Our first strategy will consist in a Diels-Alder reaction between benzyne and the 9-boraanthracene (Scheme 3.3 **A**). Our second strategy will consist in the use of our 9-aryl-9,10-dihydro-9-boraanthracene ammoniates, performing a lithiation of the benzhydryl carbon in order to perform an intramolecular nucleophilic aromatic substitution (S_NAr) onto a fluorine substituted electro-deficient aryl ring (Scheme 3.3 **B**). Finally, our third strategy, will consist in the successive addition of tris-*o*-lithiated triphenylmethane on an electrophilic boron source (Scheme 3.3 **C**).

3.2.1 First strategy : Diels-Alder reaction of benzyne over boraanthracene

Our synthesis plan starts with bis(2-bromophenyl)methane (**1**) which was described by Sparr and co-workers as a two steps synthesis from 1-iodo-2-bromobenzene with an overall yield of 70% [51]. The Grignard of the resulting bis(2-bromophenyl)methane (**1**) is then formed and mixed with dichloro dimethylsilane to form the 9-dimethyl-9,10-dihydro-9-silaanthracene (Scheme 3.4).

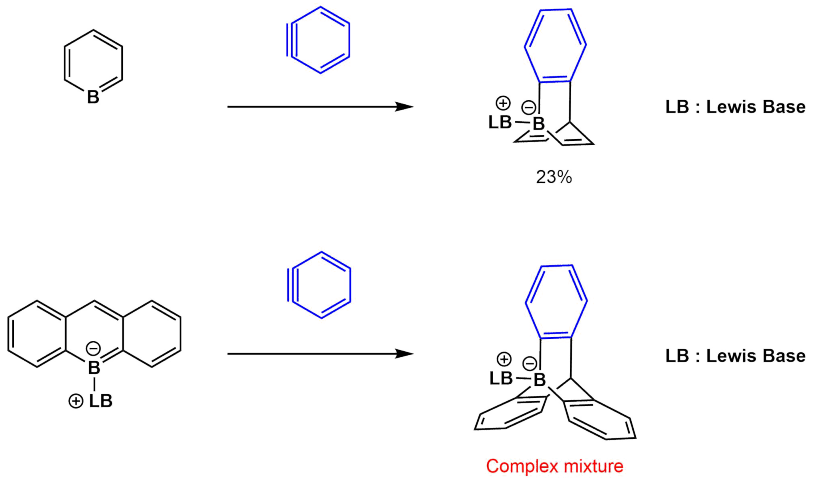


Scheme 3.3: Strategies for the synthesis of 9-boratriptycene. **A**) First strategy, **B**) Second strategy, **C**) Third strategy.



Scheme 3.4: Synthesis of 9-dimethyl-9,10-dihydro-9-silaanthracene.

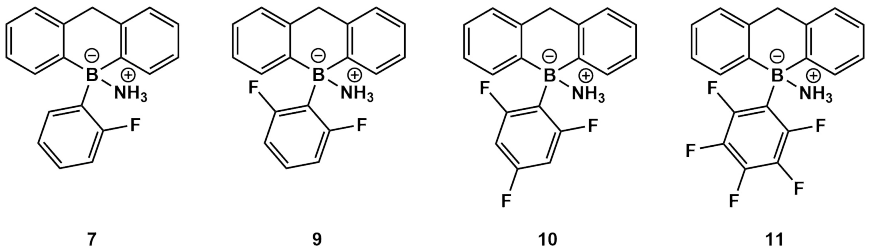
The synthesis of 9-boraanthracene which would have required other steps has been stopped at this point due to the discouraging informations discovered in the PhD. thesis of Dr. Thomas Wood, who worked on the synthesis of 9-boraanthracene stabilized by *N*-heterocyclic carbene. Indeed, a chapter of this thesis is dedicated to the synthesis of 9-boratrypticene via a Diels-Alder reaction on 9-boraanthracene. In this thesis, Wood described several attempted reaction in order to form the 9-boratriptycene but always get a complex mixture of compounds (Scheme 3.5) [59]. Considering the complex synthesis of 9-boraanthrecene and the results obtained by Wood, this strategy was abandoned at this stage to devote our attention on the two other strategies.



Scheme 3.5: Results of Diels-Alder reaction using borabenzene or 9-boraanthracene in presence of benzyne [59].

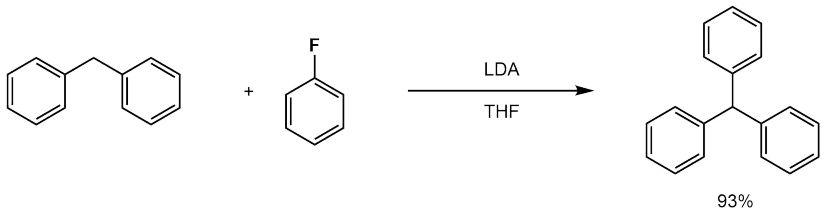
3.2.2 Second strategy : S_NAr reaction of benzhydryl carbanion on electro-deficient phenyl ring

Several fluorinated 9-aryl-9,10-dihydro-9-boraanthracene ammoniate, which have been described in the previous chapter, may be used as precursors for the synthesis of 9-boratriptycene. To allow the S_NAr reaction, the phenyl ring must be electro-deficient which is the case for 9-(2-fluorophenyl)- (**7**), 9-(2,6-fluorophenyl)- (**9**), 9-(2,4,6-fluorophenyl)- (**10**) and 9-(pentalfuorophenyl)-9,10-dihydro-9-boraanthracene ammoniate (**11**) (Scheme 3.6).



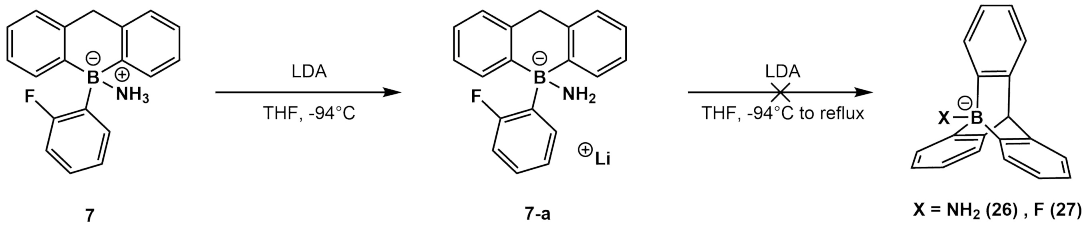
Scheme 3.6: Putative candidates for S_NAr reaction.

We choosed to keep the starting boranes in their ammonia-protected form due to the tetrahedral character of the boron atom which may facilitate the cyclisation. The reaction was first attempted with the 9-(2-fluorophenyl)-9,10-dihydro-9-boraanthracene ammoniate (**7**). Compared to the other candidates, it may seem the worst candidate to undergo an intramolecular S_NAr, but, according to Cao and co-workers, S_NAr of benzyhdryl derived carbanions on fluorobenzene is readily proceeding in presence of lithium diisopropylamine (LDA) (Scheme 3.7) [60].



Scheme 3.7: Synthesis of triphenyl methane via S_NAr of benzhydryl carbon to fluorebenzene in presence of LDA [60].

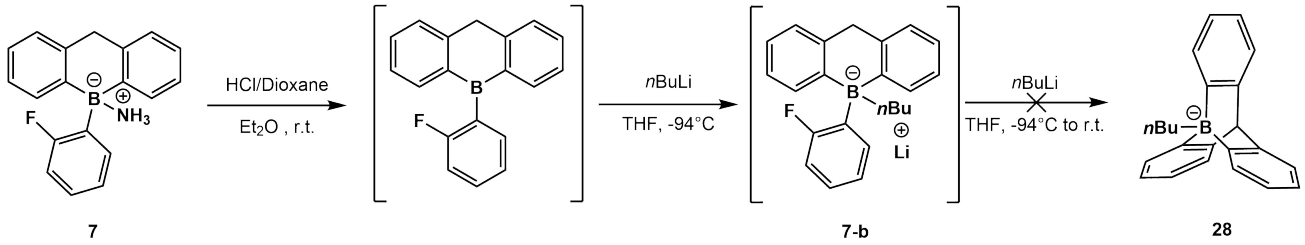
In an initial attempt, 9-(2-fluorophenyl)-9,10-dihydro-9-boraanthracene ammoniate (**7**) was treated with two equivalents of freshly prepared LDA, the deprotonation of coordinated ammonia consuming one equivalent. The reaction was in a first instance carried out for four hours at room temperature and a second time for four hours at reflux of THF. The crude reaction mixtures were analysed by ^{1}H NMR, ^{19}F NMR and ^{11}B NMR. In both cases the ^{1}H NMR only show a complex mixture while ^{11}B NMR signal was shifted from -10.3 ppm for the starting material to -8.1 for the crude product. This shows that a tetravalent boron is present in the crude product. The most relevant analysis in this case is the ^{19}F NMR. Indeed, following the mechanism of the reaction, the signal corresponding to the fluorine attached to the aryl should disappear while a signal a signal corresponding to a fluorine anion bonded to a triaryl boron compound should appear. Indeed the forming compound exhibiting stronger affinity for fluoride than ammonia, the formed borane will then bind fluoride and release ammonia. The obtained ^{19}F NMR signals are characteristics of a fluorophenyl ring. The results lead to the conclusion that the major reaction happening is simply the deprotonation of coordinated ammonia by LDA (Scheme 3.8).



Scheme 3.8: Attepted reaction to form 9-boratriptycene via intramolecular S_NAr from 9-(2-fluorophenyl)-9,10-dihydro-9-boraanthracene ammoniate **7**.

The presence of acidic protons might be problematic and induce undesired reactions. To avoid this potential issue the replacement of ammonia by a *n*butyl chain was attempted. The 9-(2-fluorophenyl)-9,10-dihydro-9-boraanthracene ammoniate (**7**) was treated with one equivalent of anhydrous hydrochloric acid in dioxane to remove ammonia via precipitation of solid ammonium chloride and after filtration and evaporation under inert conditions, the crude was reacted with two equivalents of *n*butyl lithium. Two equivalents have been used due to the addition of the first equivalent of *n*butyl lithium on the boron atom while the deprotonation of the benzhydryl carbon will occur with the second equivalent which may induce the cyclisation. As in the previous case, ^{1}H NMR gave puzzling results, while the

^{19}F and ^{11}B NMR gave clear picture. ^{19}F NMR reveals the presence of a singlet that might correspond to a fluorine atom bonded to an aryl group which reveals the absence of cyclisation. ^{11}B NMR reveals the presence of only one boron species with a chemical shift of -14.4 which might reveal that ammonia has been replaced by a butyl chain (**7-b**). As in the previous case with ammonia, no NMR signal corresponding to the 9-boratriptycene (**28**) formation have been detected. It is important to note that at this stage of the work we were not aware that hydrochloric acid in dioxane was not the best way to deprotect the borane ammoniate even if, fortunately in this case, no by product have been observed (Scheme 3.9).



Scheme 3.9: Attempted reaction to form 9-*n*butyl-9-boratriptycene (**28**) via intramolecular S_NAr from 9-(2-fluorophenyl)-9-butyl-9,10-dihydro-9-boraanthracene (**7-b**).

Two hypothesis might explain the absence of reactivity. First, as suggested before, the fluorinated aryl ring of 9-(2-fluorophenyl)-9,10-dihydro-9-boraanthracene ammoniate (**7**) is possibly no electron-deficient enough to undergo an intramolecular S_NAr reaction. Moreover, the tetravalent boron atom is electron donor which may increase the electron density on the fluorophenyl ring and disfavour the intramolecular S_NAr. The second hypothesis is highlighted by the X-ray structure of the starting material. This reveals a butterfly like shape adopted by the anthracene scaffold which is bended in the opposite direction to the additional 2-fluorophenyl ring. The structure reveals the presence of an hydrogen bond between the fluorine atom and an hydrogen bonded to the ammonia. The bond length is aroud $2{,}2$ Å and the angle formed between nitrogen, hydrogen and fluorine is about $126°$ which is characteristic of a weak hydrogen bond **??**. Even if this bond is quite weak, this interaction could contribute to direct the fluorine atom at the opposite of the benzhydryl carbon. In this position no S_NAr is allowed. Obviously, the orientation of the fluorine atom in the X-ray structure can't be the exclusive reason to explain the absence of reaction while different conformation could be adopted in solution than in the solid state.

We thus decided to attempt the S_NAr reaction with 9-(2,4,6-trifluorophenyl)-9,10-dihydro-9-boraanthracene ammoniate (**10**) which possesses a more electron deficient aryl ring with three fluorine substituents. Surprisingly, the ^{11}B NMR reveals the presence of a single compound with a chemical shift of 2.1 ppm. Those results and the X-ray structure of the starting material provides some information to explain the observed reactivity. First, the X-ray structure show that anthracene scaffold present the same butterfly shape than 9-(2-fluorophenyl)-9,10-dihydro-9-boraanthracene ammoniate

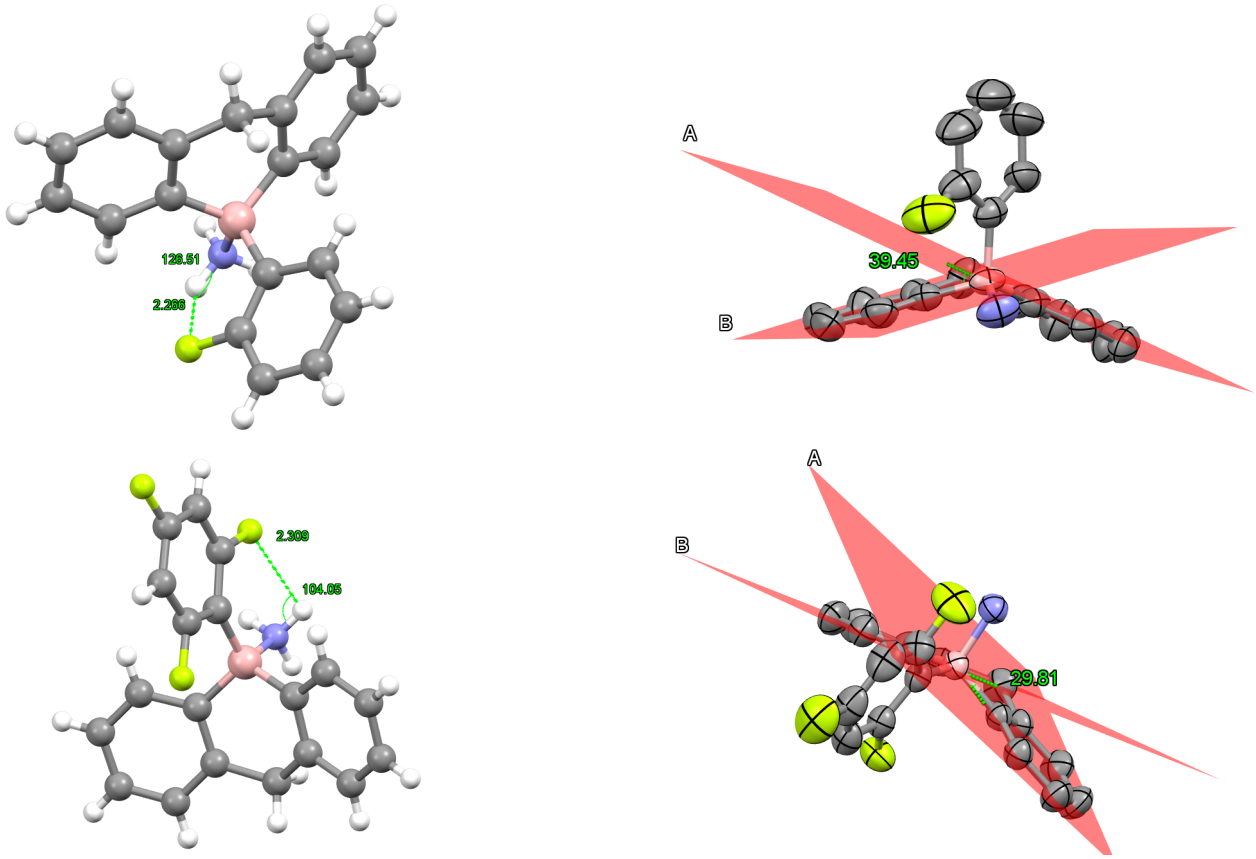
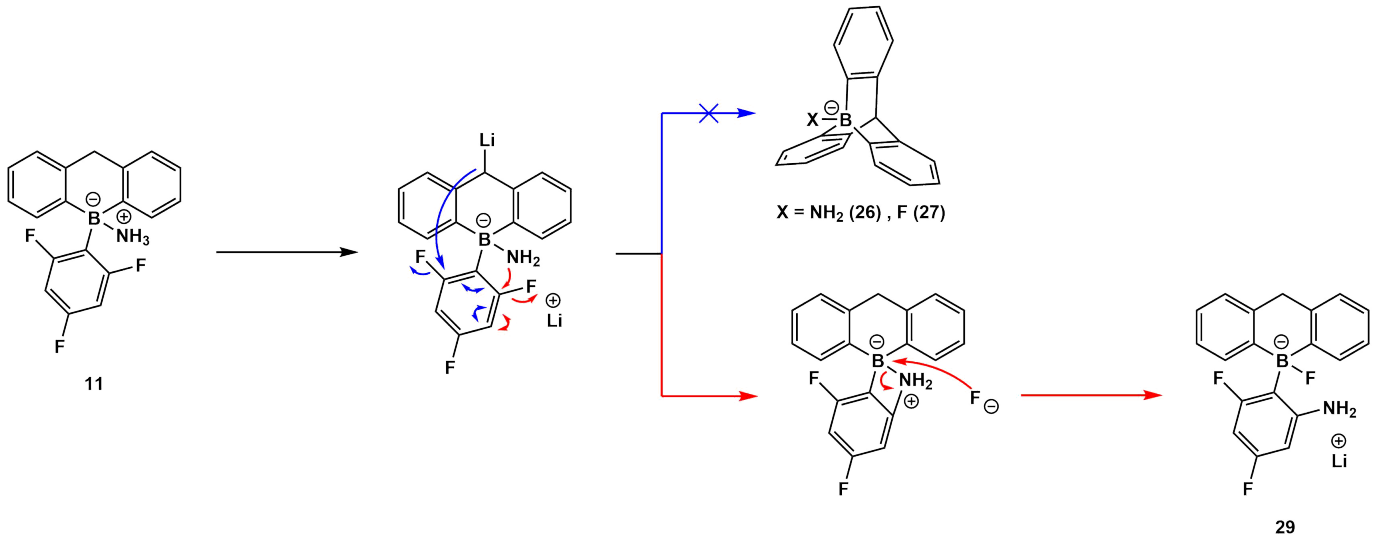


Figure 3.3: X-Ray structure of 9-(2-fluorophenyl)-9,10-dihydro-9-boraanthracene ammoniate (**7**) (above) and 9-(2,4,6-trifluorophenyl)-9,10-dihydro-9-boraanthracene ammoniate (**10**) (below).

(**7**) but bended in the opposite direction with respect to the fluorinated ring. In the 9-(2-fluorophenyl-9,10-dihydro-9-boraanthracene ammoniate (**7**) the phenyl ring faces the convex side of the anthracene structure while in the 9-(2,4,6-trifluorophenyl)-9,10-dihydro-9-boraanthracene ammoniate faces the concave side. This has an important consequence on the cyclisation of the molecule. To perform the cyclisation, the tricyclic structure has to bend in the other direction which will induce an important energy cost and disfavour the formation of the boratriptycene (Figure 3.3). The structure also reveals the presence of an hydrogen bond between one of the fluorine atom and an hydrogen of the ammonia. This hydrogen bond is also quite weak as showed by the distance between the hydrogen and fluorine of $2{,}3$ Å and the ammonia-hydrogen-fluorine angle of $104°$.

The major hypothesis to explain the apparition of the signal at 2.1 ppm in ^{11}B NMR is apparently a S_NAr reaction occurring but not from the benzhydryl lithiated carbon on the fluorophenyl ring but from the deprotonated ammonia on the fluorophenyl ring. Indeed, once deprotonated by the LDA, the ammonia has a nucleophilic lone pair that may react on the fluorophenyl ring in *ortho* position via S_NAr (Scheme 3.10) . Furthermore, as revealed by the X-ray structure, the fluorophenyl ring and the ammonia are very close which may favour the reaction.



Scheme 3.10: Proposed mechanism of the reaction of 9-(2,4,6-trifluorophenyl)-9,10-dihydro-9-boraanthracene (**11**) in presence of LDA.

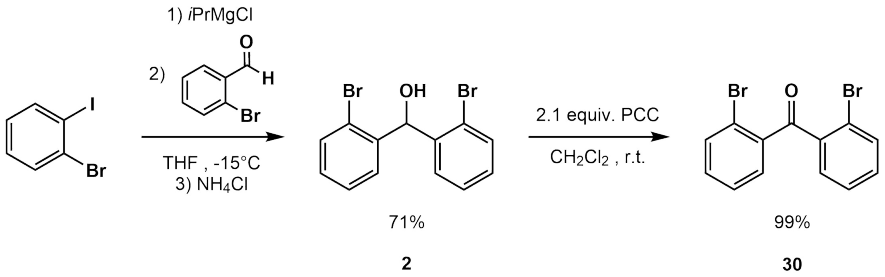
The degradation products observed after two days in open air may be explained due to the higher sensitivity of 9-fluoro-9-(2,4,6-trifluorophenyl)-9,10-dihydro-9-boraanhtracene (**29**) towards protodeborylation. The obtained results are not sufficient to prove the mechanism but if this reaction happens it might be very interesting to develop it in the context of the synthesis of frustrated Lewis pair. Indeed using a more hindered amine and removing the fluorine atom, the resulting product would be a frustrated Lewis pair. This reaction may afford a new and straightforward way to synthesize frustrated Lewis pair. However, this reaction being far from the initial topic of this research, it has not been studied in more details but will be investigated in the future. The investigations concerning this strategy have been stopped at this point due to the unexpected reactivity observed and we focused on the third and last strategy.

3.2.3 Third strategy : Consecutive additions of trislithiated triphenylmethane on an electrophilic boron source

The threefold cyclisation of a trislithiated triphenylmethane on a trivalent or tetravalent boron source have been next investigated. The synthesis of a trishalogeno-triphenylmethane is required prior to the halogen/lithium exchange.

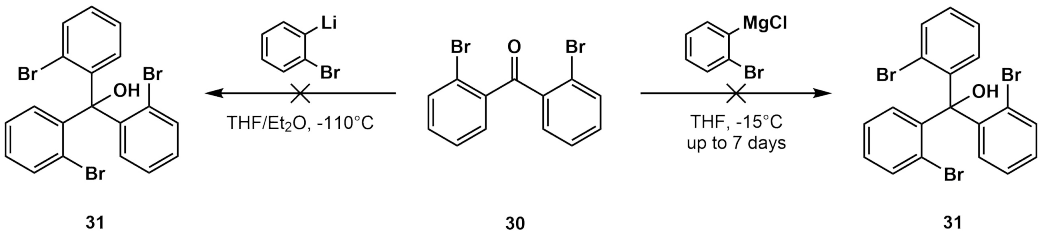
Synhtesis of tris(2-bromophenyl)- or tris(2-iodophenyl)methane

In order to attempt this strategy, tris(2-bromophenyl)-, tris(2-iodophenyl)methane or an equivalent should be synthesized. The 2,2'-dibromobenzophenone (**30**) being easily synthesized in only two steps starting from 1-iodo-2-bromobenzene, seemed to be a good precursor (Scheme 3.11) [61].



Scheme 3.11: Synthesis of 2,2'-dibromobenzophenone.

Addition of 2-bromophenyl magnesium iodide on 2,2'-dibromobenzophenone (**30**) was attempted during $3\,\mathrm{h}$ at $-15\,^{\circ}\mathrm{C}$ to avoid the formation of benzyne. In these conditions, the only product observed was the starting material. Increasing the reaction time to $8\,\mathrm{h}$ and even to seven days was not sufficient to undergo the formation of tris(2-bromophenyl)methanol (**31**), only the starting material have been observed. The reaction was then attempted using 2-bromophenyl lithium during $8\,\mathrm{h}$ at $-110\,^{\circ}\mathrm{C}$, to avoid the formation of benzyne, which did not undergo the formation of the desired product (Scheme 3.12). Considering the impossibility to keep the reaction mixture at $-110\,^{\circ}\mathrm{C}$ for an extended time, the reaction was not attempted for seven days.



Scheme 3.12: Reaction of 2,2'-dibromobenzophenone (**30**) with 2-bromophenyl lithium

In the two situations, the absence of reactivity might be explained by a combination of steric and electronic factors. The first factor is the reactivity of 2-bromophenyl magnesium bromide or lithium. First, the sterical hinderance of the two bromine atoms in ortho position decreases the rate of the reaction. Additionally, above $-15\,^{\circ}\mathrm{C}$ and $-110\,^{\circ}\mathrm{C}$ respectively the organomagnesium and organolithium derivatives are known to decompose via the formation of benzyne. To avoid the formation of benzyne, it is important to decrease the temperature which decreases the reaction kinetics. Furthermore, in the X-ray structure of the 2,2'-dibromobenzophenone (**30**) we found that the structure is completely distorted and the angle formed by the two aromatic rings is around 83° and the dihedral angle between the ketone and the aromatic ring is around 135°. This stands in contrast with an ideal case such as in benzophenone which presents a nearly planar structure with the dihedral angle formed between the two aromatic rings close to 180°. Furthermore, we found that one side of the ketone if completely hindered by the two bromine atoms while the other side is hindered by the aromatic rings. The addition of an organometallic reagent on the carbon of the ketone proceeds via an angle of 107°

which is called Bürgi-Dunitz angle. In an ideal situation, the dihedral angle between the ketone and a substituent is $180°$, the addition of a reagent via an angle of $107°$ is easy, in this case with a torsion angle of $135°$ the addition if much more complicated due to the steric hindrance.

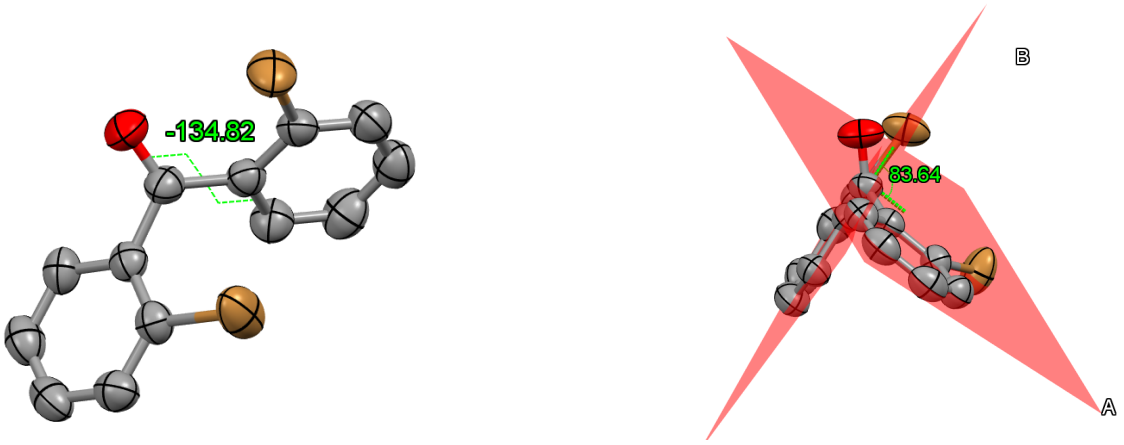
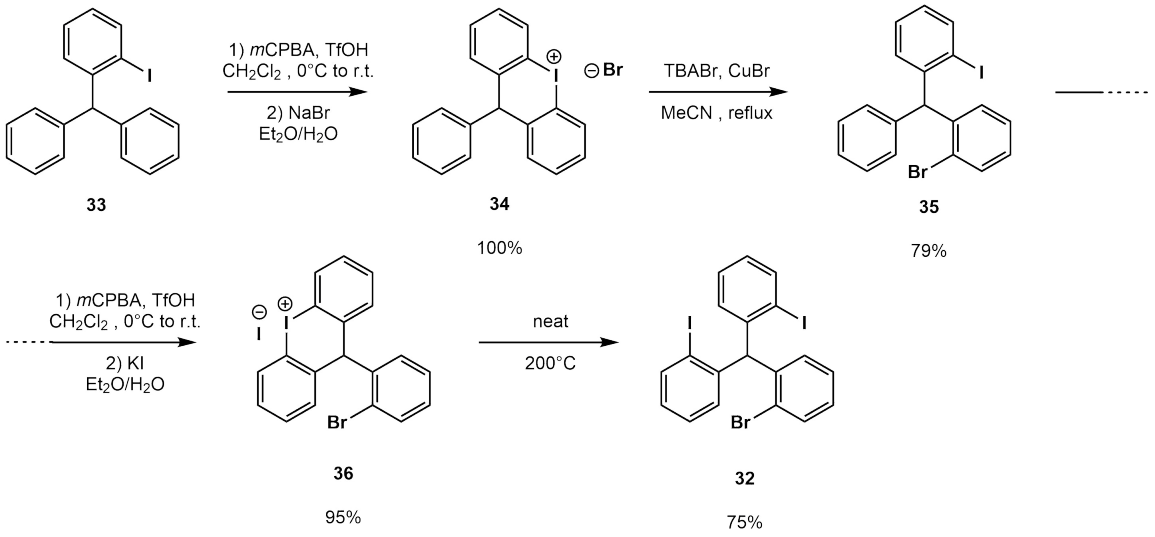


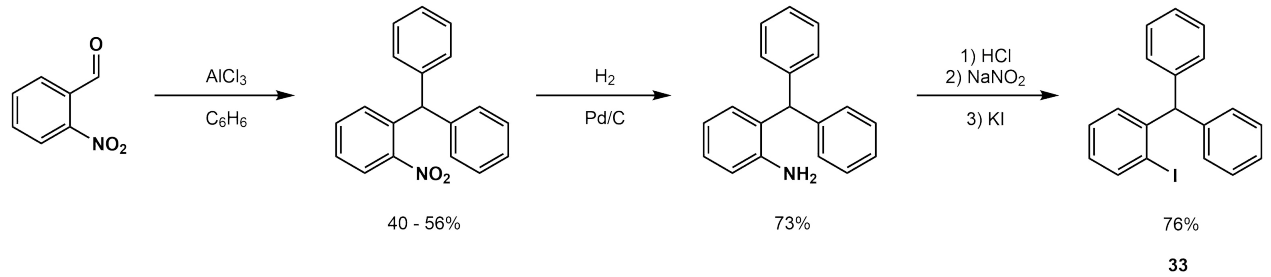
Figure 3.4: X-Ray structure of 2,2'-dibromobenzophenone (**30**). Details in experimental section

We then turned our efforts on a multistep synthesis of 2,2'-diiodo-2"-bromotriphenylmethane (**32**) reported by Peters [62]. The synthesis starts with 2-iodotriphenylmethane (**33**), which reacts with *meta*-chloro perbenzoic acid and trifluoromethane sulfonic acid to form an iodonium salt (**34**). This iodonium salt is then opened in presence of copper bromide to form the 2-iodo-2'-bromotriphenylmethane (**35**). A second iodonium salt is synthesized in the same conditions and is then opened simply by warming the compound which forms the final compound, namely 2,2'-diiodo-2"-bromotriphenylmethane (**32**) (Scheme 3.13).



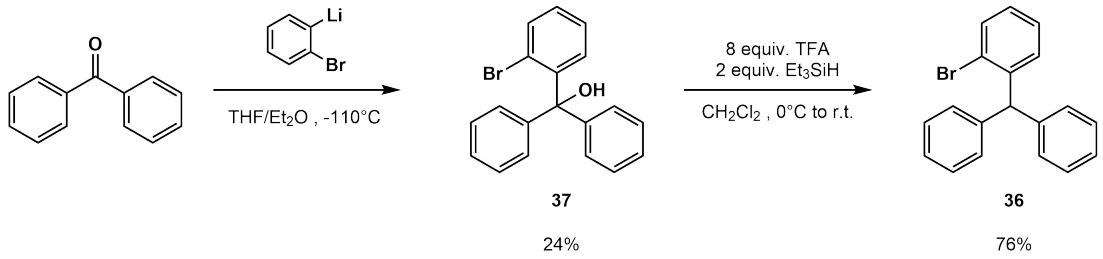
Scheme 3.13: Synhtesis of 2,2'-diiodo-2"-bromotriphenyl methane (**32**) [62]

To access the 2-iodotriphenylmethane (**33**) described as their starting material, Peters and co-workers used a three step synthesis reported Bickelhaupt and co-workers with an overall yield of 31% (Scheme 3.14)[63].



Scheme 3.14: Synthesis of 2-iodotriphenylmethane (**33**)

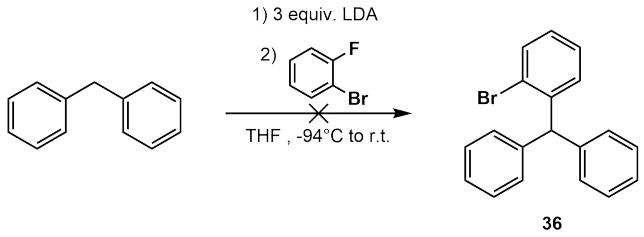
However, we preferred to synthesize 2-bromotriphenylmethane (**37**) as a precursor of 2-iodotriphenylmethane (**33**) by addition of 2-bromophenyl Grignard or lithium on benzophenone which seemed to be an interesting starting point. The reaction was, in the first instance, performed using 2-bromophenyl Grignard but 2-bromotriphenylmethanol (**38**) was obtained with poor yields between 5 and 10%. The reaction was then attempted using 2-bromophenyl lithium which provides better yields, around 25%. The 2-bromotriphenylmethanol (**38**) was then reduced using trifluoroacetic acid and triethylsilane and 2-bromotriphenylmethane (**37**) was obtained with a 76% yield (Scheme 3.15). Although the desired product was obtained, we decided to devote our attention on another synthetic pathway due to difficult purification steps.



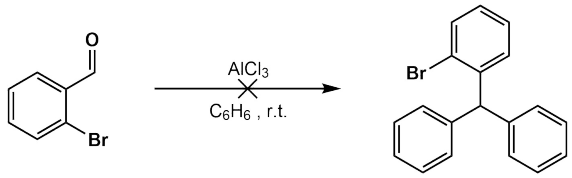
Scheme 3.15: Synthesis of 2-bromotriphenylmethane (**37**) using 2-bromophenyl lithium in presence of benzophenone

This one-step synthesis of 2-bromotriphenylmethane (**36**) was attempted using diphenylmethane and performing an S_NAr reaction over 1-bromo-2-fluorobenzene which is adapted from the work of Cao and co-workers. The results revealed a complete absence of reactivity, only the starting materials were obtained (Scheme 3.16) [60].

As presented in the procedure of Bickelhaupt and co-workers, the synthesis of 2-bromotriphenylmethane (**37**) was attempted using 2-bromobenzaldehyde in presence of aluminium trichloride and benzene [63]. The results only revealed a complex mixture (Scheme 3.17).

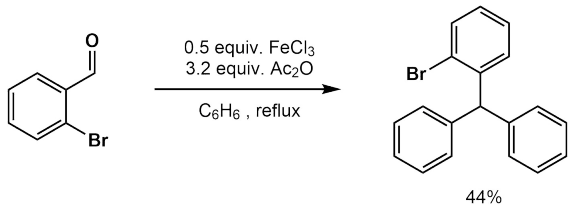


Scheme 3.16: Attempted synthesis of 2-bromotriphenylmethane (**37**) via $S_N Ar$ reaction



Scheme 3.17: Attempted synthesis of 2-bromotriphenylmethane (**37**) via Friedel-Craft reaction in presence of $\mathrm{AlCl_3}$

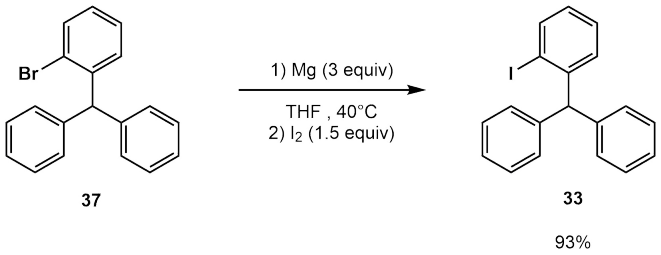
A bibliographic study revealed that Duan and co-workers described the synthesis 2,2',5,5'-dimethyl triphenylmethane using benzaldehyde and *p*-xylene in presence of iron trichloride and acetic anhydride with 79% yield [64]. This strategy was adapted using 2-bromobenzaldehyde and benzene in order to form 2-bromotriphenylmethane (**37**) (Scheme 3.18).



Scheme 3.18: Synthesis of 2-bromotriphenylmethane (**37**) using 2-bromobenzaldehyde and benzene in presence of $\mathrm{FeCl_3}$ and acetic anhydride

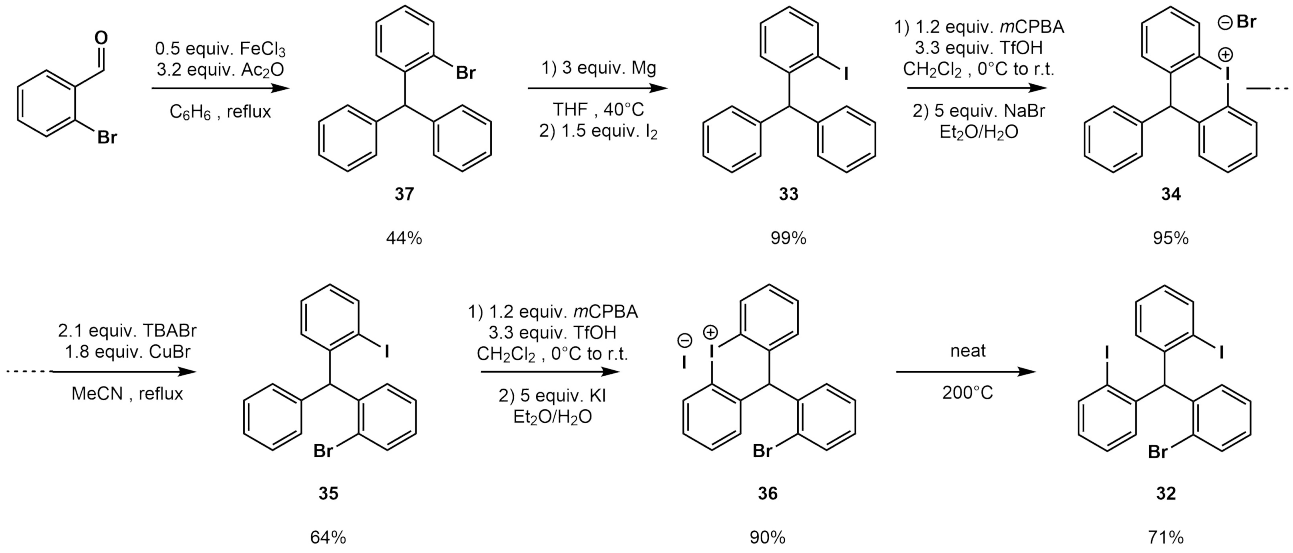
After a few optimisation step, a yield of 44% was reached. The lower yield than described in the patent may easily be explained by the use of benzene instead of *p*-xylene, benzene being much less nucleophilic than *p*-xylene. Furtermore the boiling point of *p*-xylene ($138.4°\mathrm{C}$) being much higher than benzene ($80.1°\mathrm{C}$) which allow higher reaction temperature. Even tough the yield is not so high, a large amount of product (up to $40\,\mathrm{g}$) is easily purified via silica gel chromatography, the starting material are cheap and the reaction conditions are convenient. The major advantage of this method compared to the addition of 2-bromophenyl lithium over benzophenone, is the formation of 2-bromotriphenylmethane (**37**) in a single step. It is important to note that this synthesis could also be performed using 2-iodobenzaldehyde instead of 2-bromobenzaldehyde which would provide the desired product, namely 2-iodotriphenylmethane (**33**), in a single step. Unfortunately, 2-iodobenzaldehyde is much more expensive than the brominated equivalent and a two step synthesis was preferred.

Now that a 2-bromotriphenylmethane (**37**) has been synthesized in one-step from commercially available reagents, it remained important to find a way to put an iodine atom instead of a bromine atom. The most straightforward way is to form the Grignard reagent (**37**) and then quench the reaction using iodine (Scheme 3.19). This reaction afforded **37** with a yield of 93% and the only required purification is a simple extraction.



Scheme 3.19: Synthesis of 2-iodotriphenylmethane (**33**) from 2-bromotriphenylmethane (**37**)

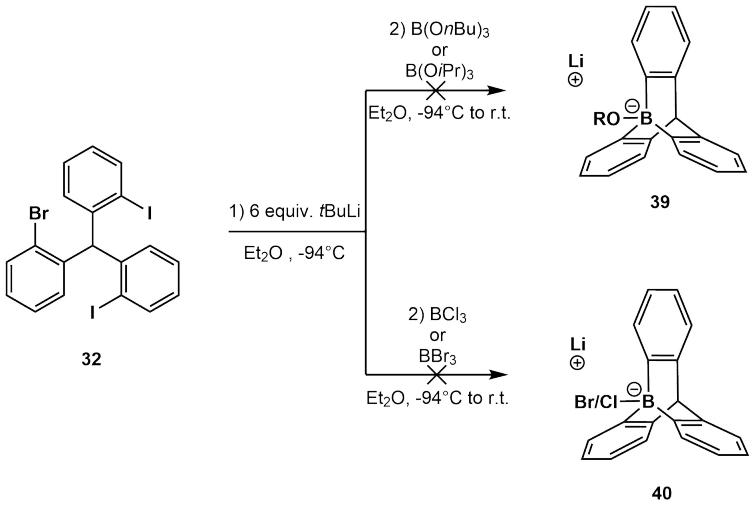
Now that the synthesis of 2-iodotriphenylmethane has been optimized, the procedure of Peters and co-workers was applied to synthesize the 2,2'-diiodo-2"-bromotriphenylmethane (**32**) [62]. The complete procedure used in this work has been performed on $40\,\mathrm{g}$ scale (Scheme 3.20).



Scheme 3.20: Optimized synthesis of 2,2'-diiodo-2"-bromotriphenylmethane (**32**)

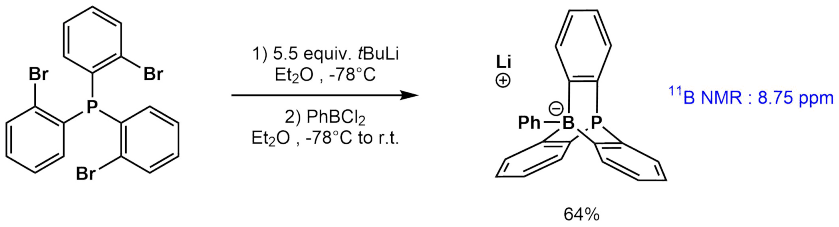
3.3 Synthesis of 9-boratriptycene

Now that a six step synthesis has been performed to synthesize the 2,2'-diiodo- 2"-bromotriphneylmethane (**32**), it remained important to use this compound to attempt the synthesis of the boratriptycene. The first borylating agent tested are the well known boron trichloride and tribromide. Peters described the synthesis of the 2,2'-diiodo-2"-bromotriphenylmethane (**32**) but also described in this paper the reaction conditions to form the tris lithiated equivalent, those conditions have been used to attempt the synthesis of boratriptycene [62]. The reaction of trilithiated triphenylmethane in presence of boron trichloride and tribromide only reveals a complex mixture and surprisingly, no signal have been observed in ^{11}B NMR (Scheme 3.21). Boron trichloride and tribromide reagents being highly electrophilic and highly reactive, they might induce many side reactions. We also employed tris*n*butyl borate and triisopropyl borate which provided the same results than using boron trichloride and tribromide (Scheme 3.21).



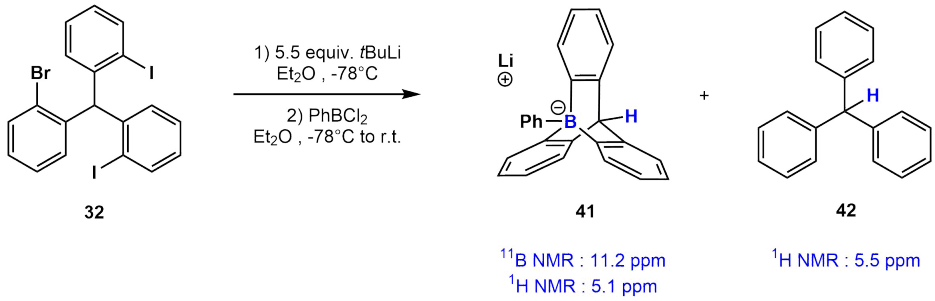
Scheme 3.21: Attempted synthesis of 9-boratriptycene using trihalogenoborane and trialkyl borate

By the time those research were carried out, Peters and co-workers published in 2018 the synthesis of 9-phosphatriptycene-10-phenylborate using tris(2-bromophenyl)phosphine and phenylboron dichloride with 64% yield (Scheme 3.22) [36]).



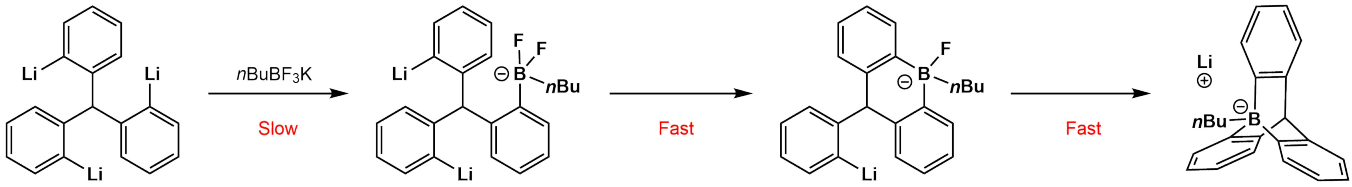
Scheme 3.22: Synthesis of 9-phosphatriptycene-10-phenylborate from tris(2-bromophenyl)phosphine in presence of $\mathrm{PhBCl_2}$ [36].

We applied this procedure, replacing tris(2-bromophenyl)phosphine by 2,2'-diiodo-2"-bromotriphenylmethane (**32**). The crude mixture was submitted to ^{11}B NMR analysis which revealed a signal at -11.2 ppm which may correspond to the 9-phenyl-9-boratriptycene (**41**), compared with the ^{11}B NMR of the 9-phosphatriptycene-10-phenylborate at -8.75 ppm. The results obtained in ^{1}H NMR revealed the presence of two signal corresponding to a trityl proton at 5.1 ppm and 5.5 ppm. The second one have been attributed to triphenylmethane (**42**) which comes from the hydrolysed trislithiated triphenylmethane while the first one to the trityl proton of 9-phenyl-9-boratriptycene (**41**) (Scheme 3.23).



Scheme 3.23: Syntheis of 9-phenyl-9-boratriptycene (**41**) from 2,2'-diiodo-2"-bromotriphenylmethane (**32**) in presence of $\mathrm{PhBCl_2}$.

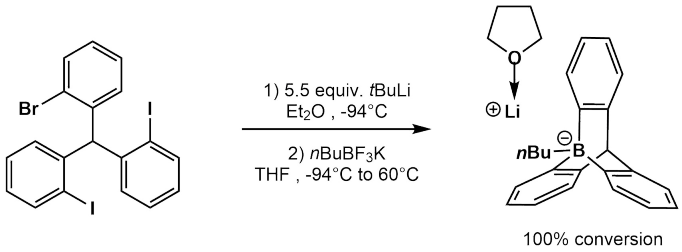
The method used for phenyl boron dichloride was adapted using potassium phenyl and *n*butyl trifluoroborate as borylating agents. Surprisingly, in these conditions, the 9-phenyl- (**41**) and 9-*n*butyl-9-boratriptycene (**28**) were detected by ^{11}B and ^{1}H NMR with a large amount of triphenylmethane showing that the reaction was not complete. No intermediate product, difluoro or monofluoro borate, were found. This is a clear insight that the first addition of aryl lithium over the borylating agent is the rate determining step and the two other addition occurs quickly (Scheme 3.24).



Scheme 3.24: Mechanism of reaction of trislithiated triphenylmethane over $n\mathrm{BuBF_3K}$

In order to reach a total conversion, the reaction conditions were slightly modified. Instead of leaving the reaction at room temperature in $\mathrm{Et_2O}$ after the addition of the borylating agent, the same quantity of THF was added and the mixture was warmed at $60\,^{\circ}\mathrm{C}$ for $48\,\mathrm{h}$. With these condition, no triphenylmethane was detected by ^{1}H NMR and only the signal corresponding to 9-*n*butyl-9-boratriptycene (**28**) was obtained. Even though if the conversion was quantitative, no yield have been determined due to the presence of THF coordinated to the lithium countercation even after evaporation

for several days under dynamic vacuum (Scheme 3.25 and Figure 3.5). Furthermore in these conditions, the compound turns out to be highly hygroscopic, the exact mass is then impossible to determine.



Scheme 3.25: Synthesis of 9-*n*butyl-9-boratriptycene (**28**) with lithium as counter cation

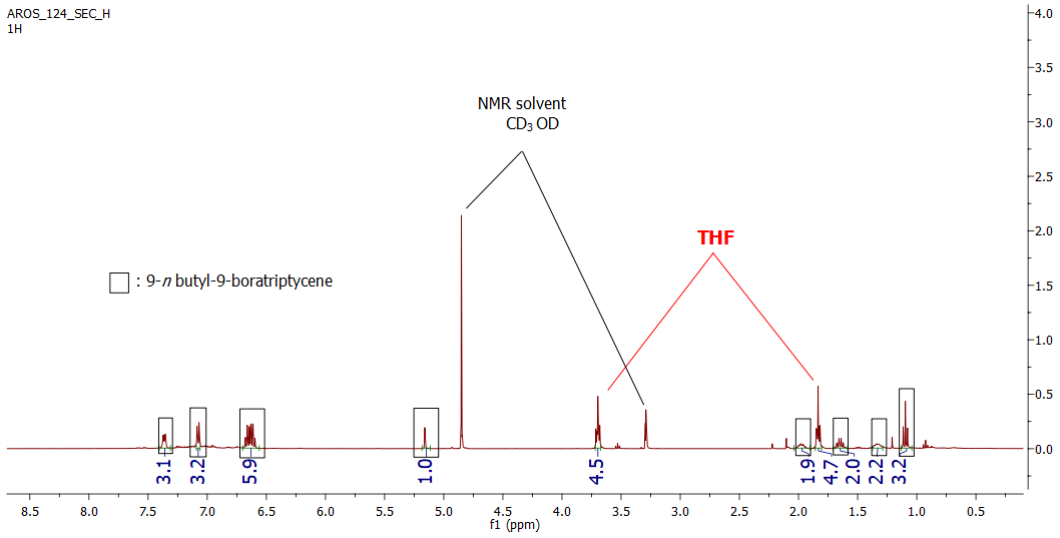


Figure 3.5: ^{1}H NMR of 9-*n*butyl-9-boratriptycene (**28**) with lithium as counter cation

In order to purify the product a cation exchange has been performed using tetramethylammonium chloride (TMACl). The 9-*n*butyl-9-boratriptycene tetramethyl ammonium salt (**43**) have been obtained with high purity and was crystallized to provide crystals suitable for X-ray analysis. The X-ray structure of 9-*n*butyl-9-boratriptycene tetramethyl ammonium salt (**43**) (Figure 3.6 and Table 3.1) may be compared to the one of 9-phosphatriptycene-10-*n*butylborate obtained by a co-worker of our group (Figure 3.6 and Table 3.1). The pyramidalisation of the boron atom is even more pronouced than in the phosphaboratriptycene with a mean angle formed by the boron atom and the three phenyl rings of $101{,}6°$ in comparison to $104.6°$ respectively. The geometric differences between the two triptycene are due to the larger size of phosphorus atom than the carbon. Another important feature is the distance between the boron atom and the plane formed by C(6)-C(12)-C(18) for the phospaboratriptycene and C(1)-C(13)-C(14) for the boratritycene (**43**). This distance illustrates perfectly the pyramidalisation of the boron atom and is respectively of 0.674Å and 0.734Å. The pyramidalisation of the boron atom

being related to the Lewis acidity our data highlights the potential of boratriptycene to be a more powerful Lewis acid than phosphaboratriptycene.

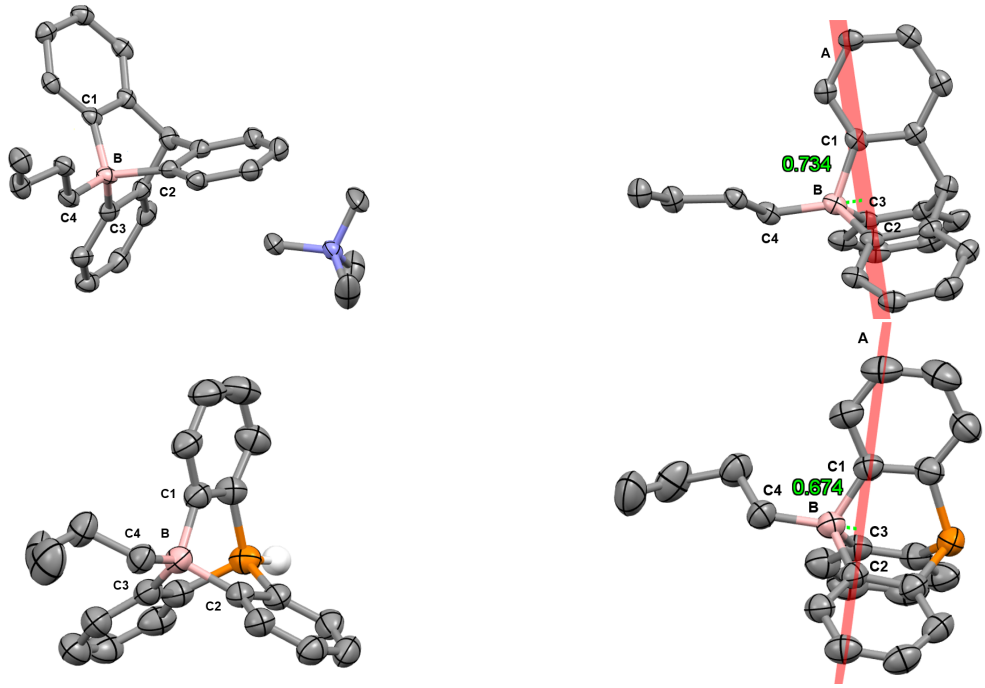


Figure 3.6: X-Ray structure of 9-*n*butyl-9-boratriptycene tetramethyl ammonium salt (**43**) (above) and 9-phopshatriptycene-10-*n*butylborate (below) with ellipsoid diagram (50%) and hydrogen atom omitted.

Table 3.1: Important distances and angles values of 9-boratriptycene and 9-phosphatriptycene-10-phenylborate

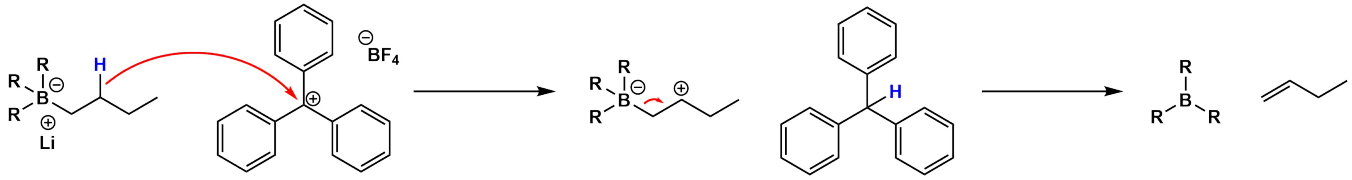
	9-boratriptycene (**43**)		9-phosphatriptycene-10-phenylborate	
Distances (Å)	**C**(1)-**B**(1)	1.649(5)	**C**(1)-**B**(1)	1.655(2)
	C(2)-**B**(1)	1.652(4)	**C**(2)-**B**(1)	1.661(2)
	C(3)-**B**(1)	1.641(4)	**C**(3)-**B**(1)	1.653(2)
	C(4)-**B**(1)	1.611(5)	**C**(4)-**B**(1)	1.624(2)
	A-**B**(1)	0.734	**A**-**B**(1)	0.674
Angles (°)	**C**(1)-**B**-**C**(2)	102.4(2)	**C**(1)-**B**-**C**(2)	103.9(1)
	C(1)-**B**-**C**(3)	101.6(2)	**C**(1)-**B**-**C**(3)	107.2(1)
	C(1)-**B**-**C**(4)	116.4(3)	**C**(1)-**B**-**C**(4)	113.2(1)
	C(2)-**B**-**C**(3)	101.0(2)	**C**(2)-**B**-**C**(3)	102.6(1)
	C(2)-**B**-**C**(4)	117.7(3)	**C**(2)-**B**-**C**(4)	113.5(1)
	C(3)-**B**-**C**(4)	115.3(3)	**C**(3)-**B**-**C**(4)	115.1(1)

3.4 Deprotection of 9-R-9-boratriptycene

The 9-*n*butyl-9-boratriptycene (**43**) being synthesized, it was important to keep in mind that the final objective remained the deprotection of the boron atom to form the trivalent boron. In order to maximize the chances of deprotection, several protecting groups were considered as well as different deprotection method. Each strategy involved the synthesis of a 9-boratriptycene carrying a different protecting group on the boron atom.

3.4.1 Removal of the *n*butyl chain

The removal of a *n*butyl chain from a tetravalent boron compound by a tritylium cation is already known [65]. This proceeds via hydride abstraction followed by a β-elimination and breaking of the C-B bond to generate 1-butene as a gas and release the trivalent 9-boratriptycene. (Scheme 3.26).

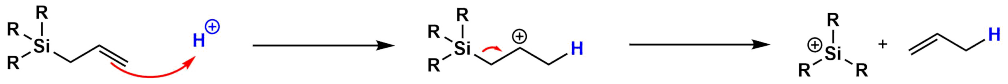


Scheme 3.26: β-elimination of a *n*butyl chain from a tetravalent boron atom in presence of tritylium cation

After mixing one equivalent of tritylium tetrafluoroborate with 9-*n*butyl-9-boratriptycene (**43**) in $CDCl_3$, the ^{11}B NMR spectrum only revealed the presence of the starting reagents. This may be explained by the poor solubility of the two compound in $CDCl_3$ added with the probable slow rate of the reaction. This reaction is also described at high temperature which has not been tested in our case.

3.4.2 Synthesis of 9-allyl-9-boratriptycene and removal of allyl chain

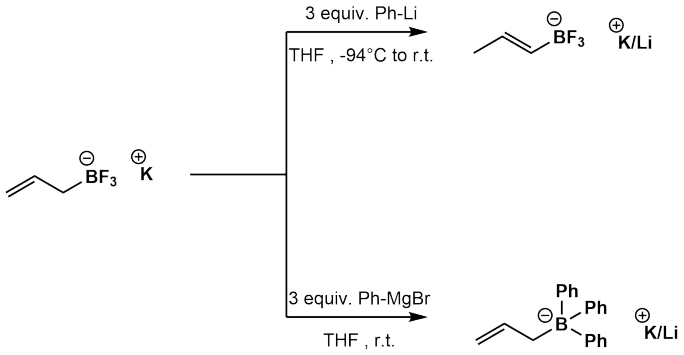
Allyl substituents are well known precursors for the synthesis of super electrophilic silylium cations. In a presence of a strong Bronsted acid, consecutive protonation of the allyl followed by β-elimination which release 1-propene afford a sililium cation (Scheme 3.27) [66].



Scheme 3.27: Sililium cation synthesis via β-elimination of protonated allyl chain

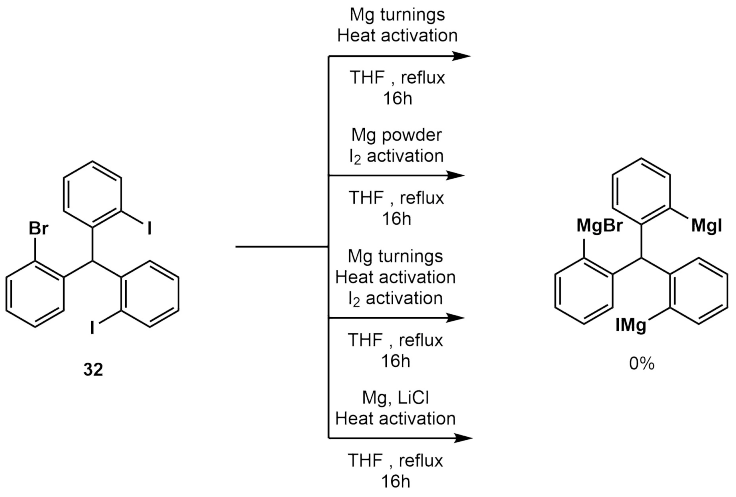
A trivalent boron being isoelectronic to a sililium cation, the 9-allyl-9-boratriptycene might be deprotected using a strong Bronsted acid. Therefore, the synthesis of 9-allyl-9-boratriptycene was attempted following the same procedure as described before, using potassium allyl trifluoroborate

instead of *n*butyl trifluoroborate. Surprisingly, the ^{1}H and ^{11}B NMR revealed the presence of triphenylmethane (**42**) and the complete absence of desired product. Furthermore, a signal corresponding to allyl trifluoroborate was detected in ^{1}H NMR but corresponded to the isomerized product, meaning that a deprotonation occured in α-position of the allyl function. In order to confirm this hypothesis, two control reaction have been performed. First, potassium allyl trifluoroborate was put in presence of three equivalents of phenyl lithium and with three equivalents of phenyl magnesium bromide in a second instance. Using three equivalents of phenyl lithium, the NMR analysis revealed the same results as observed using trislihtiated triphenylmethane, no addition of a phenyl lithium on the boron atom have been detected. On the other side, the reaction with three equivalents of phenyl magnesium bromide revealed the formation of *n*butyl triphenylborate which highlight the potential of a grignard reagent to add on allyl trifluoroborate (Scheme 3.28).



Scheme 3.28: Reaction of phenyl lithium and phenyl magnesium bromide over potassium allyltrifluoroborate

Following these results, the reaction of 2,2'-diiodo-2"-bromotriphenylmethane (**32**) with preactivated magnesium was attempted in order to form the Grignard reagent. Surprisingly, the starting material remained unchanged after $3\,\mathrm{h}$ at room temperature. The magnesium was activated by various methods (high temperature and high vacuum, addition of iodine crystal) and the reaction was performed for different times (3 to $16\mathrm{h}$) at various temperatures (room temperature to reflux) in THF which provided the same results. Finally, the reaction was attempted using preactivated magnesium and lithium chloride, to form Grignard reagent in the condition of Knochel [67]. Surprisingly, this method provided the same results (Scheme 3.29). Therefore the formation of Grignard from 2,2'-diiodo-2"-bromotriphenylmethane (**32**) sesms very difficult. The synthesis of 9-allyl-9-boratriptycene stoped at this point, the reaction being too difficult using potassium allyl trifluoroborate and 2,2'-diiodo-2"-bromotriphenylmethane (**32**).



Scheme 3.29: Attempted formation of 2,2'-diiodo-2"-bromotriphenylmethane grignard equivalent

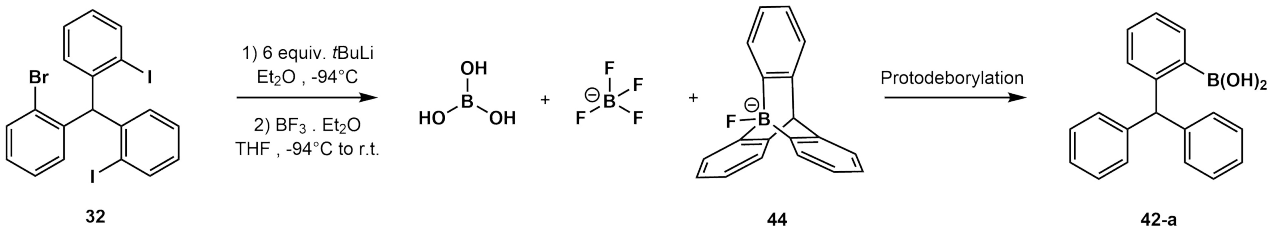
3.4.3 Synthesis of 9-fluoro-9-boratriptycene (44) and removal of fluorine

Another potential precursor for the synthesis of 9-boratriptycene is the 9-fluoro-9-boratriptycene (**44**). Addition of antimony pentafluoride which is a Lewis acid showing a very high affinity for fluoride anion should result in the abstraction of the fluorine atom. Indeed antimony pentafluoride is known as one of the compound that exhibits the highest affinity for fluoride anion [68]. If the antimony is unable to remove the fluoride anion, it will mean that 9-boratriptycene is a Lewis superacid, even stronger than antimony pentafluoride and it will be extremely difficult to obtain in the trivalent form.

The same procedure as described before was then performed using potassium tetrafluoroborate as borylating agent. The ^{1}H NMR revealed the formation of a complex mixture and the ^{11}B NMR only revealed the presence of boric acid which suggests a degradation of the tetrafluoroborate. The ^{19}F NMR confirmed a complete absence of tetrafluoroborate anion in the crude product but revealed a signal at -75.9 ppm which could correspond to the 9-fluoro-9-boratriptycene (**44**).

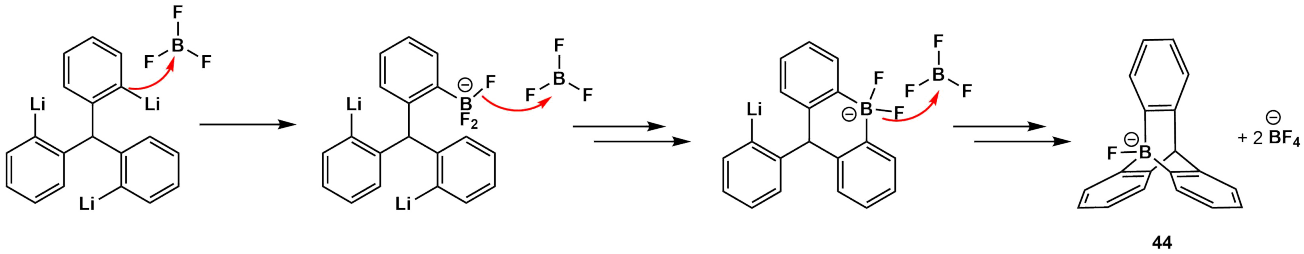
The reaction was then attempted using boron trifluoride etherate complex, which exhibit higher electrophilicity than potassium tetrafluoroborate, following the same experimental conditions [69]. The ^{11}B and ^{19}F NMR results were quite intriguing, it revealed the presence of boric acid and tetrafluoroborate while the ^{1}H NMR revealed the presence of two signals at 5.5 ppm, typical of triphenylmethane and 5.1 ppm, probably the 9-fluoro-9-boratriptycene (**44**). The intensity of the signal in ^{11}B NMR corresponding to tetrafluoroborate may hide the signal corresponding to 9-fluoro-9-boratriptycene (**44**). The crude was then mixed with dichloromethane and filtered in order to remove boric acid and tetrafluoroborate salts and the filtrate was evaporated and further submitted to ^{1}H,

^{11}B and ^{19}F NMR. A signal at -75.8 ppm that was already present in the crude product but hidden by the intensity of tetrafluoroborate appeared. This doublet may reveal the presence of a fluorine atom bonded to a boron atom due to the ^{19}F-^{11}B coupling. The ^{11}B NMR analysis only revealed the presence of boronic acid (**42-a**), no signal corresponding to 9-fluoro-9-boratriptycene (**44**) have been detected which may be due to the very low concentration of this product. A new signal appeared in ^{1}H NMR at 5.3 ppm which may correspond to a trityl proton. The appearance of this signal in ^{1}H NMR combined with the appearance of boronic acid (**42-a**) in ^{11}B NMR may confirm the formation of 9-fluoro-9-boratriptycene (**44**) which undergo rapid deborylation (Scheme 3.30).



Scheme 3.30: Probable reaction of trislithiated triphenylmethane in presence of $BF_3 \cdot Et_2O$

Two important features remain unexplained, namely the formation of tetrafluoroborate while the reaction is performed using boron trifluoride etherate and the degradation of tetrafluoroborate into boric acid. A possible explanation for the formation of tetrafluoroborate anion is depicted in Scheme 3.31.



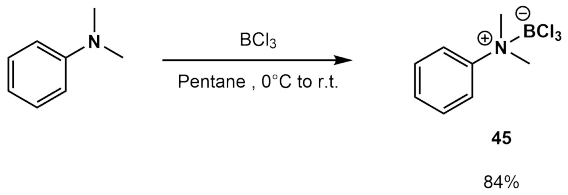
Scheme 3.31: Proposed mechanism for the reaction of trislithiated triphenylmethane in presence of $BF_3 \cdot Et_2O$

The trislithiated triphenylmetane add on trifluoroborate to form an aryl trifluoroborate. The corresponding acid of this newly formed compound, phenyl difluoroborate, may be less Lewis acidic than BF_3. Consequently, another molecule of BF_3 may remove a fluoride atom from phenyl trifluoroborate to form tetrafluoroborate anion and phenyl difluoroborate. The same reaction happens after the second addition, but not after the third addition, the 9-boratriptycene formed having a higher affinity for fluorine than BF_3. The decomposition of tetrafluoroborate anion into boric acid remained unexplained.

Considering the previous results, the reaction was attempted several times but the desired product being unstable, it remained impossible to purify 9-fluoro-9-boratriptycene. This strategy was then stopped at this point.

3.4.4 Synthesis of amino protected 9-boratriptycene and removal of amino group

Considering the issues presented in the different attempted synthesis such as the need of counter cation exchange or the issues due to the deprotection, a most practical synthesis as to be found. In order to avoid the issues due to ions pairs, the reaction was attempted using dimethylaniline trichloroborate as borylating agent in the standard condition, described before. Using this compound as borylating agent, the 9-dimethylaniline-9-boratriptycene formed would remain globally electronically neutral, which may facilitate the purification. The dimethylaniline trichloroborate (**45**) has been simply synthesize mixing dimethylaniline and boron trichloride (Scheme 3.32) [70].

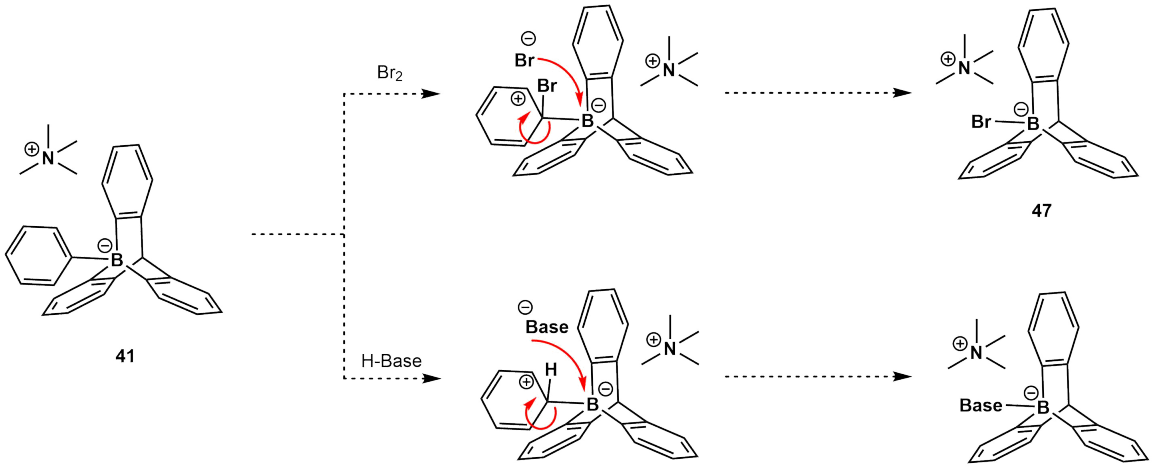


Scheme 3.32: Synthesis of dimethylaniline boron trichloride complex (**45**)

The crude product of the reaction was submitted to ^{1}H and ^{11}B NMR analysis, which surprisingly revealed an absence of signal in ^{11}B NMR and a complex mixture in ^{1}H NMR with a total absence of signal corresponding to the resulting 9-dimethylaniline-9-boratriptycene. The reaction was then attempted using triethylamine boron trichloride (**46**) which has been prepared in the same conditions as dimethylaniline boron trichloride complex (**45**). The results were exactly identical which doesn't provide any information about the reaction. This strategy stopped at this stage and the research time came to an end, the synthesis of 9-boratriptycene stopped at this stage.

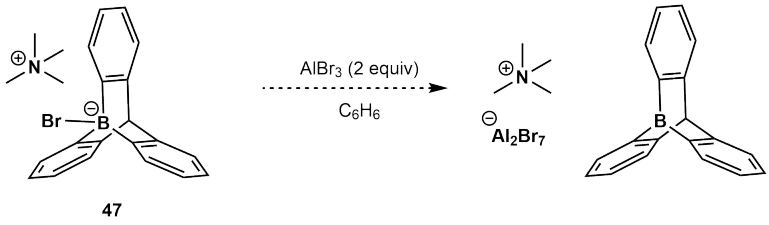
3.5 Conclusion and perspectives

Our goal to develop a method to synthesize the 9-boratriptycene in its trivalent form has been nearly reached. Indeed an efficient method to form the tetravalent 9-aryl- or 9-alkyl-boratriptycene has been achieved but the protecting group on the tetravalent boron atom has not been removed. In perspective, the obtention of 9-boratriptycene via the cleavage of the phenyl-B bond of 9-phenyl-9-boratriptycene (**41**) can be considered and has already been observed in our group with a phosphorus analogue during this work. We are confident that we will be able to remove the phenyl ring by oxidation, protonation in Brönsted acidic conditions or bromination in presence of dibromine (Scheme 3.33) [71].



Scheme 3.33: Proposed method to deprotect the 9-phenyl-9-boratriptycene (**41**)

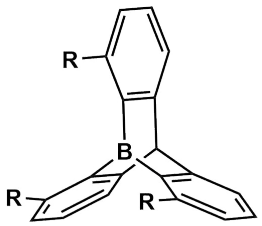
In the two cases, if the 9-boratriptycene turns out to be one of the strongest known boron Lewis acid, it would react with the conjugated base of the Brönsted acid, or the bromide anion to form 9-bromo-9-boratriptycene (**47**). In those case, the 9-boratriptycene would remain protected but this time a more specific Lewis acids might be used. For exemple in the case of 9-bromo-9-boratriptycene (**47**), the product may be mixed with two equivalents of aluminium tribromide which exhibit a good affinity for bromide anion, and result in the formation of 9-boratriptycene and the formation of non coordinating anion $Al_2Br_7^-$ with a countercation NMe_4^+. (Scheme 3.34).



Scheme 3.34: Deprotection of 9-bromo-9-boratriptycene with aluminium tribromide

In the future, if the 9-boratriptycene turns out to be as predicted as extraordinary strong boron Lewis acid, it might be used to activate $C-F$ or $C-H$ bond and will allow the development of new reactions

in the field of metal-free catalysis. Furthermore, considering its predicted Lewis acidic properties, this compound would probably react with nearly all Lewis bases, it might then be interesting to add several hindered substituents in *ortho*-position of the boron atom. We already started the synthesis of the 2,2'-diiodo-2"-bromotriphenylmethane with 3-methyl- subsituents on each phenyl ring but the desired compound has not been obtained so far. With bulky substituents in *ortho*-position of the boron atom, the reactivity of the 9-boratriptycene may be tuned and it may find very important applications in the context of frustrated Lewis pairs (Figure 3.7).



R = Me, *i*Pr, *t*Bu

Figure 3.7: Sterically hindered 9-boratriptycene as boron Lewis acid in frustrated Lewis pair catalysis

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APPENDIX **A**

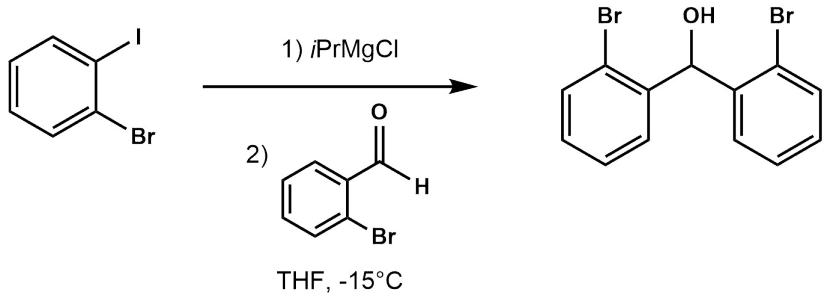
Experimental section

General considerations

The flasks were dried using heating gun and usual Schlenk methods. THF, CH_2Cl_2 and Et_2O were dried with a solvent purification system. Solvents, reagents and chemicals were purchased from Sigma-Aldrich, Carbosynth, FluoroChem, ABCR and TCI and used without further purification, except for potassium phenyl trifluoroborate and potassium *n*butyl trifluoroborate which have been recrystallized in hot acetone. All the NMR samples were prepared in standard 5 mm borosilicate tubes at room temperature (between 18 and 22 $^{\circ}\mathrm{C}$) by diluting the sample in deuterated solvents. Spectra were resolved with MestReNova program. Spectra were recorded on a JEOL JNM EX-400 and the chemical shifts (δ) are given in ppm. The references considered as 0.0 ppm are tetramethylsilane (TMS) for ^{1}H NMR and ^{13}C , trifluoroborate etherate ($BF_3.Et_2O$) for ^{11}B NMR and trichloromonofluoromethane ($CFCl_3$) for ^{19}F NMR.

Single-crystal diffraction data of all molecules were collected on a Oxford Diffraction Gemini Ultra R system (4-circle kappa platform, Ruby CCD detector) using Mo Kα radiation ($\lambda = 0.71073$Å). The structures solved by SHELXT and then refined by full-matrix least-squares refinement of F using SHELXL-2016. Non-hydrogen atoms were refined anisotripically; hydrogen atoms were located from a difference Fourier map. Hydrogen atoms not involved in hydrogen bonding were refined in the riding mode with isotropic temperature factors fixed at 1.2U of the parents atoms (1.5U for methyl group). Coordinates of the hydrogen atoms implicated in hydrogen bonds were refined. The program Mercury was used for molecular graphics.

*Synthesis of bis(2-bromophenyl)methanol (**2**)*



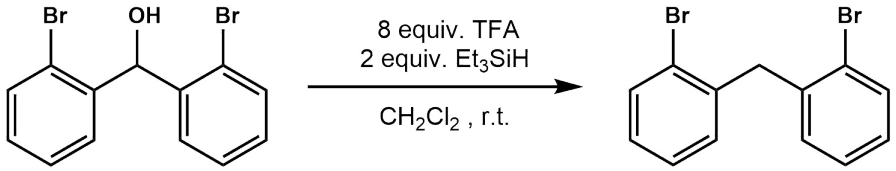
Prepared according to a litterature procedure [1]. Under Ar atmosphere, a solution of *i*PrMgCl ($2{,}0\,\mathrm{mol\,dm^{-3}}$, $117\,\mathrm{mL}$, $117\,\mathrm{mmol}$, 1.0 equiv.) in THF was added to a 1-iodo-2-bromobenzene (30.0 mL, $234\,\mathrm{mmol}$, 1.0 equiv.) solution in THF ($200\,\mathrm{mL}$) at $-20\,^{\circ}\mathrm{C}$ for $1.5\,\mathrm{h}$. The mixture was stirred at $-15\,^{\circ}\mathrm{C}$ for $1{,}5\,\mathrm{h}$. At the same temperature, 2-bromobenzaldehyde ($24\,\mathrm{mL}$, $206\,\mathrm{mmol}$, 0.88 equiv.) was added over $45\,\mathrm{min}$. The mixture was stirred at $-15\,^{\circ}\mathrm{C}$ for further $45\,\mathrm{min}$. Saturated aqueous NH_4Cl ($100\,\mathrm{mL}$) and H_2O ($700\,\mathrm{mL}$) were added and the reaction mixture was allowed to warm at room temperature. The mixture was diluted with Et_2O, the organic phase was collected and the aqueous phase was extracted using Et_2O ($2 * 200\,\mathrm{mL}$). The combined organic layers were dried over $MgSO_4$ and then filtered. The crude mixture was concentrated under reduced pressure. Precipitation into hexane following by filtration afforded bis(2-bromophenyl)methanol as a white powder. ^{1}H and ^{13}C NMR data are in good aggreament with the one reported in the literature.

Yield: $55.7\mathrm{g}$, 79%

^{1}H NMR ($400\mathrm{MHz}$, $CHCl_3$-d^1) δ (ppm)= 7.57 (dd, $J = 7.8$, $J = 1.0\mathrm{Hz}$, 2 H), $7.28 - 7.34$(m, 4 H), 7.18 (ddd, $J = 7.9, 6.9$, $J = 2.2\mathrm{Hz}$, 2 H), 6.40(d, $J = 4.1$ Hz, 1 H), 2.61 (d, $J = 4.2$ Hz, 1 H)

^{13}C NMR ($100\mathrm{MHz}$, $CHCl_3$-d_1) δ (ppm)= 140.9, 132.9, 129.4, 128.7, 127.6, 123.8, 74.2

*Synthesis of bis(2-bromophenyl)methane (**1**)*



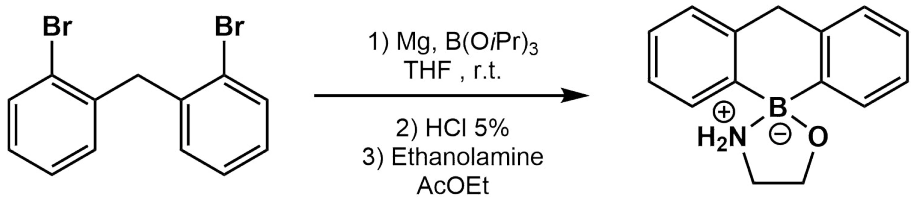
Prepared according to the literature [2]. Trifluoroacetic acid ($36.0\mathrm{mL}$, $469\,\mathrm{mmol}$, 8 equiv.) was added dropwise to a solution of bis(2-bromophenyl)methanol ($20.1\mathrm{g}$, $58.8\mathrm{mmol}$, 1 equiv.) in CH_2Cl_2 ($150\,\mathrm{mL}$) at $0\,^{\circ}\mathrm{C}$. The mixture was stirred at $0\,^{\circ}\mathrm{C}$ for $5\,\mathrm{min}$. At the same temperature, triethylsilane ($19\,\mathrm{mL}$, $119\,\mathrm{mmol}$, 2 equiv.) was added dropwise. The mixture was allowed to warm at room temperature and stirred overnight. The crude mixture was concentrated under reduce pressure. Filtration through a plug of silica gel following by evaporation to dryness afforded the title compound as a colorless oil. ^{1}H and ^{13}C NMR data are in good aggreament with the one reported in the literature.

Yield: $19.0\mathrm{g}$, 99%

^{1}H NMR ($400\mathrm{MHz}$, $CHCl_3$-d_1) δ (ppm)= 7.61 (dd, J = 7.9 Hz, 2 H), 7.23 (td, J = 7.5, 1.3 Hz, 2 H), 7.12 (td, $J = 7.7, 1.8$ Hz, 2 H), 6.99 (dd, $J = 7.6, 1.6$ Hz, 2 H), 4.21 (s, 2 H)

^{13}C NMR ($100\mathrm{MHz}$, $CHCl_3$-d^1) δ (ppm)= 139.0, 133.0, 130.8, 128.2, 127.7, 125.2, 42.2

*Synthesis of 9-aminoethoxy-9,10-dihydro-9-boraanthracene (**3**)*



Under Ar atmosphere, bis(2-bromophenyl)methane ($5.1\,\mathrm{g}$, $15.6\,\mathrm{mmol}$, 1 equiv.) was mixed with tributylborate ($4.2\,\mathrm{mL}$, $15.6\,\mathrm{mmol}$, 1 equiv.) and THF ($40\,\mathrm{mL}$) in a dropping funnel and added over thermally preactivated magnesium turnings ($1.14\,\mathrm{g}$, $46.7\,\mathrm{mmol}$, 3 equiv.) over $1\,\mathrm{h}$ at constant $20\,^{\circ}\mathrm{C}$. The mixture was left stirring at $20\,^{\circ}\mathrm{C}$ for $72\,\mathrm{h}$. Hydrochloric acid ($1.5\,\mathrm{mol\,dm^{-3}}$, $50\,\mathrm{mL}$) was added. The organic phase was collected and the aqueous phase was extracted using ethyl acetate ($3 * 20\,\mathrm{mL}$). The combined organic layers were dried over $MgSO_4$ and then filtered. The solution was concentrated under reduced pressure. Ethyl acetate ($20\,\mathrm{mL}$) and ethanolamine ($0.94\,\mathrm{mL}$, $15.6\,\mathrm{mmol}$, 1 equiv.) was added. The mixture was stirred at room temperature overnight. The crude mixture was concentrated under reduced pressure. Precipitation into DCM following by filtration afforded 9-aminoethoxy-9,10-dihydro-9-boraanthracene as an off-white powder.

Yield: $2.7\,\mathrm{g}$, 75%

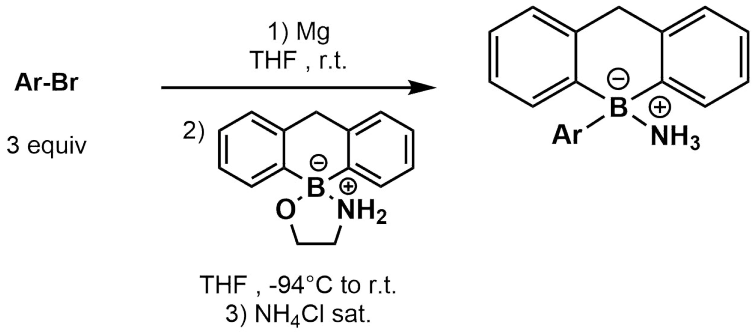
Crystals suitable for X-ray structure analysis have been obtained by slow evaporation of saturated solution of 9-aminoethoxy-9,10-dihydro-9-boraanthracene in methanol.

^{1}H NMR ($400\,\mathrm{MHz}$, DMSO-d_6) δ (ppm)= 7.53-7.79 (m, 2 H), 7.19-7.15 (m, 2 H), 7.10-7.04 (m, 4 H), 5.52 (br s, 2 H), 4.11 (t, $J = 6.1$ Hz, 2 H), 3.89 (AB, $J = 77.5, 17.1$ Hz, 2 H), 2.86 (t, $J = 6.1$ Hz, 2 H)

^{13}C NMR ($100\,\mathrm{MHz}$, DMSO-d^6) δ (ppm)= 149.2, 143.5, 130.8, 126.6, 125.8, 124.9, 65.2, 60.2, 42.8, 41.7.

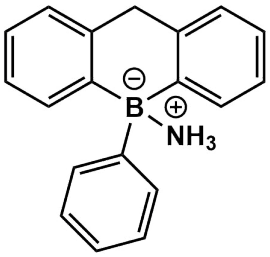
^{11}B NMR ($160\,\mathrm{MHz}$, DMSO-d^6) δ (ppm)= -0.2

General procedure A for synthesis of 9-aryl-9,10-dihydro-9-boraanthracene ammoniate



Under Ar atmosphere, a solution of bromo- or chloro-aryl as mentionned (3 equiv.) in THF ($0.5\mathrm{mmol\,mL^{-1}}$) was added over magnesium turnings (4 equiv.). The mixture is stirred $2\,\mathrm{h}$ at room temperature. At $-94\,^{\circ}\mathrm{C}$, the above Grignard solution was transferred dropwise into a THF ($0{,}5\,\mathrm{mmol\,mL^{-1}}$) solution of 9-aminoethoxy-9,10-dihydro-9-boraanthracene (1 equiv). The mixture was stirred at $-94\,^{\circ}\mathrm{C}$ for $2\,\mathrm{h}$ then allowed to warm at room temperature overnight. Excess of saturated aqueous NH_4Cl was added. The mixture is stirred at room temperature for $30\,\mathrm{min}$. The organic phase was collected and the aqueous phase was extracted using ethyl acetate ($3 * 30\,\mathrm{mL}$). The combined organic layers were dried over $MgSO_4$ and then filtered. The crude mixture was concentrated under reduce pressure. Precipitation into hexane following by filtration afforded 9-aryl-9,10-dihydro-9-boraanthracene ammoniate as a white powder.

*Synthesis of 9-phenyl-9,10-dihydro-9-boraanthracene ammoniate (**5**)*



The title compound was prepared according to general procedure A with 9-aminoethoxy-9,10-dihydro-9-boraanthracene ($400\,\mathrm{mg}$, $1.69\mathrm{mmol}$), 1-bromobenzene ($0.53\mathrm{mL}$, $5.06\mathrm{mmol}$, 3.7 equiv.) and magnesium turnings ($200\,\mathrm{mg}$, $8.22\mathrm{mmol}$). 9-phenyl-9,10-dihydro-9-boraanthracene ammoniate ($198\,\mathrm{mg}$, $0.73\mathrm{mmol}$, 43.3%) was isolated as a white powder after purification by precipitation using hexane as solvent.

"One pot" procedure : Under Ar atmosphere, bis(2-bromophenyl)mehtane ($2.00\mathrm{g}$, $6.19\mathrm{mmol}$, 1 equiv.) was mixed with phenyl-tributylborate ($1.9\mathrm{g}$, $6.19\mathrm{mmol}$, 1 equiv.) and THF ($20\,\mathrm{mL}$) in a dropping funnel and added over magnesium turnings ($450\,\mathrm{g}$, $18.5\mathrm{mmol}$, 3 equiv.) over $30\,\mathrm{min}$ at constant $20\,^{\circ}\mathrm{C}$. The mixture was left stirring at $20\,^{\circ}\mathrm{C}$ for $48\,\mathrm{h}$. Saturated aqueous NH_4Cl ($50\,\mathrm{mL}$) was added. The organic phase was collected and the aqueous phase was extracted using ethyl acetate ($3 * 20\,\mathrm{mL}$). The combined organic layers were dried over $MgSO_4$ and then filtered. The solution was concentrated under reduced pressure. Precipitation into hexane following by filtration afforded 9-phenyl-9,10-dihydro-9-boraanthracene ammoniate ($0.72\mathrm{mg}$, 43.0%) as a white powder.

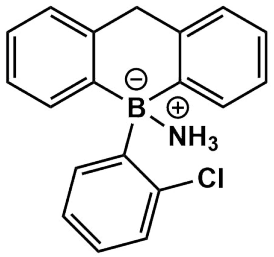
Crystals suitable for X-ray structure analysis have been obtained by slow evaporation of saturated solution of 9-phenyl-9,10-dihydro-9-boraanthracene ammoniate in methanol.

^{1}H NMR ($400\mathrm{MHz}$, CH_3OH-d^4) δ (ppm)$=$ 7.56 (d, $J = 7.1$ Hz, 2 H), 7.12-7.02 (m, 6 H), 6.96 (dd, $J = 14.6$, 7.3 Hz, 4 H), 6.91-6.82 (m, 1 H), 5.65 (br, 3 H), 3.68 (AD, $J = 16.7$ Hz, 2 H).

^{13}C NMR ($100\mathrm{MHz}$, CH_3OH-d^4) δ (ppm)$=$ 141.9, 133.0, 130.4, 128.8, 126.3, 124.9, 124.5, 31.2

^{11}B NMR ($160\mathrm{MHz}$, CH_3OH-d^4) δ (ppm)$=$ -9.6 (br s)

*Synthesis of 9-(2-chlorophenyl)-9,10-dihydro-9-boraanthracene ammoniate (**6***



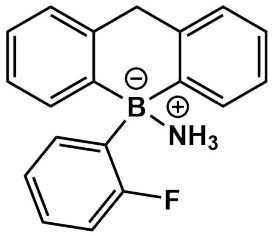
The title compound was prepared according to the general procedure A with 9-aminoethoxy-9,10-dihydro-9-boraanthracene ($1.24\mathrm{g}$, $5.22\mathrm{mmol}$), 1-bromo-2,6-difluorobenzene ($1.9\mathrm{mL}$, $16.3\mathrm{mmol}$) and magnesium turnings ($500\,\mathrm{mg}$, $20.6\mathrm{mmol}$). 9-(2-chlorophenyl)-9,10-dihydro-9-boraanthracene ammoniate ($796\,\mathrm{mg}$, $2.61\mathrm{mmol}$, 50.0%) was isolated as a pale yellow powder after purification by precipitation using hexane as solvent.

^{1}H NMR ($400\mathrm{MHz}$, acetone-d^6) δ (ppm)= 7.52-7.38 (m, 2 H), 7.16-7.11 (m, 1 H), 7.03-6.88 (m, 7 H), 5.49 (br, 3 H), 3.86 (s, 2 H).

^{13}C NMR ($100\mathrm{MHz}$, acetone-d^6) δ (ppm)= 142.5, 135.4, 130.8, 129.2, 126.7, 126.3, 125.1, 124.7, 124.5

^{11}B NMR ($160\mathrm{MHz}$, acetone-d^6) δ (ppm)= -8.8 (br s)

*Synthesis of 9-(2-fluorophenyl)-9,10-dihydro-9-boraanthracene ammoniate (**7**)*



The title compound was prepared according to the general procedure A with 9-aminoethoxy-9,10-dihydro-9-boraanthracene ($3.00\mathrm{g}$, $12.7\mathrm{mmol}$), 1-iodo-2-fluorobenzene ($5.21\mathrm{mL}$, $44.6\mathrm{mmol}$, 3.5 equiv.) and magnesium turnings ($1.20\mathrm{g}$, $49.5\mathrm{mmol}$). 9-(2-fluorophenyl)-9,10-dihydro-9-boraanthracene ammoniate ($2.09\mathrm{g}$, $5.68\mathrm{mmol}$, 44.9%) was isolated as a pale yellow powder after purification by precipitation using hexane as solvent.

Crystals suitable for X-ray structure analysis have been obtained by slow evaporation of a saturated solution of 9-(2-fluorophenyl)-9,10-dihydro-9-boraanthracene ammoniate in methanol.

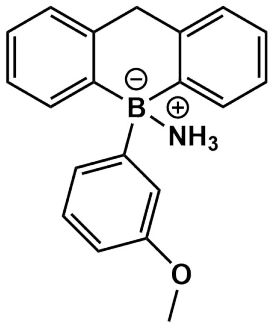
^{1}H NMR ($400\mathrm{MHz}$, CH_3OH-d^4) δ (ppm)= 7.48(d, $J = 7.1$ Hz, 2 H), 7.08 (d, $J = 7.1$ Hz, 2 H), 7.06-6.92 (m, 5 H), 6.77-6.71 (m, 2 H), 6.61 (d, $J = 7.2$, 1.7 Hz, 1 H), 5.66 (br, 2 H), 3.81-3.66 (m, 2 H)

^{13}C NMR ($100\mathrm{MHz}$, CH_3OH-d^4) δ (ppm)= 142.1, 135.3 (d, $J = 12.6$ Hz), 131.0 (d, $J = 1.8$ Hz), 127.1 (d, $J = 8.2$ Hz), 126.4, 124.8 (d, $J = 5.7$ Hz), 123.1 (d, $J = 2.4$ Hz), 114.5, 114.2, 67.5.

^{11}B NMR ($160\mathrm{MHz}$, CH_3OH-d^4) δ (ppm)= -10.3 (br s)

^{19}F NMR ($377\mathrm{MHz}$, CH_3OH-d^4) δ (ppm)= -103.5 (br, 1 H).

*Synthesis of 9-(3-anisole)-9,10-dihydro-9-boraanthracene ammoniate (**8**)*



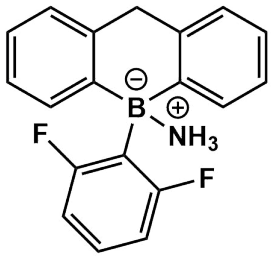
The title compound was prepared according to the general procedure A with 9-aminoethoxy-9,10-dihydro-9-boraanthracene ($700\,\mathrm{mg}$, $2.95\mathrm{mmol}$), 3-bromoanisole ($1.1\mathrm{mL}$, $8.69\mathrm{mmol}$) and magnesium turnings ($400\,\mathrm{mg}$, $16.5\mathrm{mmol}$). 9-(3-anisole)-9,10-dihydro-9-boraanthracene ammoniate ($441\,\mathrm{mg}$, $1.46\mathrm{mmol}$, 49.5%) was isolated as a pale yellow powder after purification by precipitation using hexane as solvent.

^{1}H NMR ($400\mathrm{MHz}$, CH_3OH-d^4) δ (ppm)= 7.45 (dd, $J = 7.2$, 0.9 Hz, 2 H), 7.13-7.06 (m, 2 H), 7.04-6.98 (m, 2 H), 6.97-6.94 (m, 1 H), 6.72 (dt, $J = 7.2$, 0.9 Hz, 1 H), 6.69-6.66 (m, 1 H), 3.76 (br, 2 H), 3.60 (s, 3 H).

^{13}C NMR ($100\mathrm{MHz}$, CH_3OH-d^4) δ (ppm)= 158.5, 142.2, 129.3, 127.1, 125.8, 125.3, 124.3, 124.2, 120.8, 118.1, 53.9, 40.2

^{11}B NMR ($160\mathrm{MHz}$, CH_3OH-d^4) δ (ppm)= -9.5 (br s)

*Synthesis of 9-(2,6-difluorophenyl)-9,10-dihydro-9-boraanthracene ammoniate (**9**)*



The title compound was prepared according to the general procedure A with 9-aminoethoxy-9,10-dihydro-9-boraanthracene ($502\,\mathrm{mg}$, $2.11\mathrm{mmol}$), 1-bromo-2,6-difluorobenzene ($0.72\mathrm{mL}$, $6.42\mathrm{mmol}$) and magnesium turnings ($200\,\mathrm{mg}$, $8.22\mathrm{mmol}$). 9-(2,6-difluorophenyl)-9,10-dihydro-9-boraanthracene ammoniate ($299\,\mathrm{mg}$, $0.97\mathrm{mmol}$, 46.0%) was isolated as a pale yellow powder after purification by precipitation using hexane as solvent.

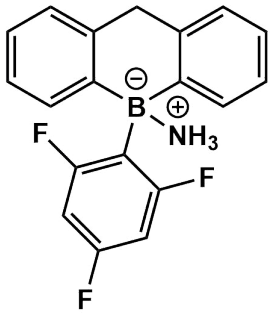
^{1}H NMR ($400\mathrm{MHz}$, DMSO-d^6) δ (ppm)= 7.48 (d, J = 7.1 Hz, 2 ,H), 7.08 (d, J = 7.1 Hz, 2 H), 7.06-6.92 (m, 5 H), 6.77-6.71 (m, 2 H), 6.61 (td, J = 7.1, 1.7 Hz, 1 H), 5.57 (br, 2 H), 3.81-3.67 (m, 2 H).

^{13}C NMR ($100\mathrm{MHz}$, DMSO-d^6) δ (ppm)= 165.6, 142.1 (d, J = 1.0 Hz), 135.3 (t, J = 7.6 Hz), 131.1 (d, J = 4.8 Hz), 127.1 (d, J = 8.0 Hz), 126.4, 124.8 (d, J = 3.9 Hz), 123.1 (d, J = 2.3 Hz), 114.6 (d, J = 26.3 Hz).

^{11}B NMR ($160\mathrm{MHz}$, DMSO-d^6) δ (ppm)= -10.3 (br s)

^{19}F NMR ($377\mathrm{MHz}$, DMSO-d^6) δ (ppm)= -103.5 (d, J = 5.2 Hz, 2 F).

*Synthesis of 9-(2,4,6-trifluorophenyl)-9,10-dihydro-9-boraanthracene ammoniate (**10**)*



The title compound was prepared according to the general procedure A with 9-aminoethoxy-9,10-dihydro-9-boraanthracene (1.01g, 4.22mmol), 1-bromo-2,4,6-trifluorobenzene (1.5mL, 12.7mmol) and magnesium turnings (400 mg, 16.5mmol). 9-(2,4,6-trifluorophenyl)-9,10-dihydro-9-boraanthracene ammoniate (516 mg, 1.59mmol, 37.6%) was isolated as a yellow powder after purification by precipitation using hexane as solvent.

Crystals suitable for X-ray structure analysis have been obtained by slow evaporation of a saturated solution of 9-(2,4,6-trifluorophenyl)-9,10-dihydro-9-boraanthracene ammoniate in methanol.

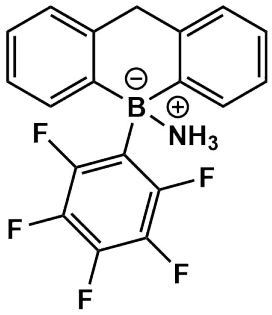
^{1}H NMR (400MHz, CH_3OH-d^4) δ (ppm)= 7.24-7.17 (m, 4 H), 7.12-7.03 (m, 4 H), 6.60-6.52 (m, 2 H), 4.37 (br, 3 H), 4.21-4.05 (m, 2 H)

^{13}C NMR (100MHz, CH_3OH-d^4) δ (ppm)= 141.5, 131.9, 126.9, 125.7, 125.0, 117.3, 99.0

^{11}B NMR (160MHz, CH_3OH-d^4) δ (ppm)= -9.8 (br s)

^{19}F NMR (377MHz, CH_3OH-d^4) δ (ppm)= -100.3 (br, 2 F), -116.0 (br, 1 F)

*Synthesis of 9-(pentafluorophenyl)-9,10-dihydro-9-boraanthracene ammoniate (**11**)*



The title compound was prepared according to the modified general procedure A with 9-aminoethoxy-9,10-dihydro-9-boraanthracene ($1.25\mathrm{g}$, $5.25\mathrm{mmol}$), 1-chloro-pentafluorobenzene ($2.5\mathrm{mL}$, $19.4\mathrm{mmol}$, 3.7 equiv.) and magnesium turnings ($500\,\mathrm{mg}$, $20.6\mathrm{mmol}$). The dropwise addition of the solution of 1-chloro-pentafluorobenzene in THF over magnesium turnings was performed at $0\,^{\circ}\mathrm{C}$ and the reaction was stirred at $0\,^{\circ}\mathrm{C}$ for $3\,\mathrm{h}$. 9-(pentafluorophenyl)-9,10-dihydro-9-boraanthracene ammoniate ($907\,\mathrm{mg}$, $2.51\mathrm{mmol}$, 47.8%) was isolated as a color solid after purification by precipitation using hexane as solvent.

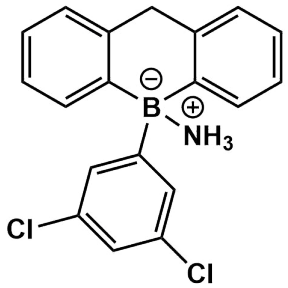
^{1}H NMR ($400\mathrm{MHz}$, CH_3OH-d^4) δ (ppm)= 7.29-7.22 (m, 2 H), 7.13 (d, J = 7.1 Hz, 2 H), 7.06-6.94 (m, 4 H), 4.37 (br, 3 H), 4.03 (AB, J = 20.7, 11.7 Hz, 2 H).

^{13}C NMR ($100\mathrm{MHz}$, CH_3OH-d^4) δ (ppm)= 141.9, 132.4, 126.8, 125.6, 125.0

^{11}B NMR ($160\mathrm{MHz}$, CH_3OH-d^4) δ (ppm)= -10.5 (br s).

^{19}F NMR ($377\mathrm{MHz}$, CH_3OH-d^4) δ (ppm)= -165.1 (br, 1 F), -160.6 (br, 2 F), -131.1 (br, 2 F)

*Synthesis of 9-(3,5-dichlorophenyl)-9,10-dihydro-9-boraanthracene ammoniate (**12**)*



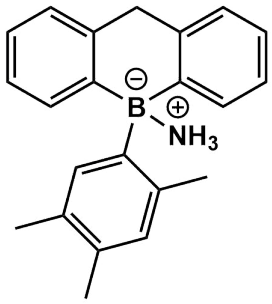
The title compound was prepared according to the general procedure A with 9-aminoethoxy-9,10-dihydro-9-boraanthracene ($400\,\mathrm{mg}$, $1.68\mathrm{mmol}$), 1-iodo-3,5-dichlorobenzene ($1.36\mathrm{g}$, $5.90\mathrm{mmol}$) and magnesium turnings ($200\,\mathrm{mg}$, $8.22\mathrm{mmol}$). 9-(3,5-dichlorophenyl)-9,10-dihydro-9-boraanthracene ammoniate($120\,\mathrm{mg}$, $0.35\mathrm{mmol}$, 21.0%) was isolated as an orange powder after purification by precipitation using hexane as solvent.

Crystals suitable for X-ray structure analysis have been obtained by slow evaporation of saturated solution of 9-(3,5-dichlorophenyl)-9,10-dihydro-9-boraanthracene ammoniate in methanol.

^{1}H NMR ($400\mathrm{MHz}$, MeOH-d^4) δ (ppm)$=$ 7.50-7.37 (m, 2 H), 7.20-7.09 (m, 4 H), 7.20-7.09 (m, 2 H), 7.01-6.95 (m, 2 H), 3.85-3.65 (m, 2 H)

^{11}B NMR ($160\mathrm{MHz}$, MeOH-d^4) δ (ppm)$=-10.1$ (br s)

*Synthesis of 9-(2,4,5-trimethylphenyl)-9,10-dihydro-9-boraanthracene ammoniate (**13**)*



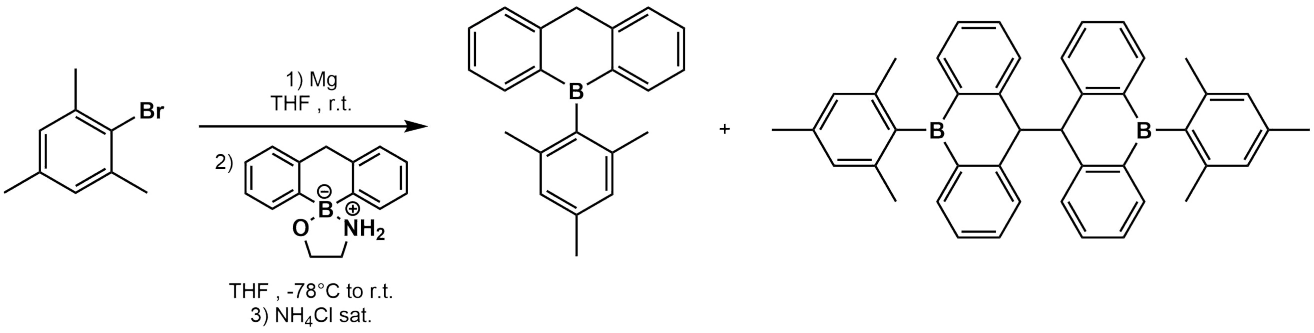
The title compound was prepared according to the general procedure A with 9-aminoethoxy-9,10-dihydro-9-boraanthracene ($700\,\mathrm{mg}$, $2.95\mathrm{mmol}$), 1-bromo-2,6-difluorobenzene ($1.81\mathrm{g}$, $9.09\mathrm{mmol}$) and magnesium turnings ($400\,\mathrm{mg}$, $16.5\mathrm{mmol}$). 9-(2,4,5-trimethylphenyl)-9,10-dihydro-9-boraanthracene ammoniate ($245\,\mathrm{mg}$, $0.79\mathrm{mmol}$, 26.6%) was isolated as a white powder after purification by precipitation using hexane as solvent.

^{1}H NMR ($400\mathrm{MHz}$, MeOH-d^4) δ (ppm)$=$ 7.14 (d, $J = 7.4$ Hz, 3 H), 7.00 (ddd, $J = 10.4$, 8.8, 4.3 Hz, 4H), 6.90 (t, $J = 7.2$ Hz, 2 H), 6.62 (s, 1 H), 4.35-3.93 (m, 2 H), 2.29 (s, 3 H), 2.18 (s, 3 H), 1.34 (s, 3 H).

^{13}C NMR ($100\mathrm{MHz}$, MeOH-d^4) δ (ppm)$=$ 141.8, 139.0, 132.4, 132.1, 131.0, 130.4, 126.3, 124.6, 124.4.

^{11}B NMR ($160\mathrm{MHz}$, MeOH-d^4) δ (ppm)$=$ -9.3 (br s)

*Synthesis of 9-mesityl-9,10-dihydro-9-boraanthracene (**14**) and the corresponding dimer (**15**)*



Under Ar atmosphere, a solution of bromomesitylene ($2.6\mathrm{mL}$, $17.0\mathrm{mmol}$, 3.4 equiv) in THF ($15\,\mathrm{mL}$) was added over magnesium turnings ($500\,\mathrm{mg}$, $20.6\mathrm{mmol}$, 4 equiv.). The mixture is stirred $2\,\mathrm{h}$ at room temperature. At $-94\,^{\circ}\mathrm{C}$, the above Grignard solution was transferred dropwise into a THF ($10\,\mathrm{mL}$) solution of 9-aminoethoxy-9,10-dihydro-9-boraanthracene ($1.17\mathrm{g}$, $4.93\mathrm{mmol}$, 1 equiv.). The mixture was stirred at $-94\,^{\circ}\mathrm{C}$ for $2\,\mathrm{h}$ then allowed to warm at room temperature overnight. Excess of saturated aqueous NH_4Cl was added. The mixture is stirred at room temperature for $30\,\mathrm{min}$. The organic phase was collected and the aqueous phase was extracted using ethyl acetate ($3 * 30\,\mathrm{mL}$). The combined organic layers were dried over $MgSO_4$ and then filtered. The crude mixture was concentrated under reduce pressure. Precipitation into hexane following by filtration afforded the dimer of 9-mesityl-9,10-dihydro-9-boraanthracene as a white powder. The filtrate was concentrated under reduce pressure. Purification by silica gel chromatography using hexane as solvant afforded 9-mesityl-9,10-dihydro-9-boraanthracene as colorless crystals.

9-mesityl-9,10-dihydro-9-boraanthracene (**14**) : Yield: $387\,\mathrm{mg}$, 26.5%

Crystals suitable for X-ray structure analysis have been obtained by slow evaporation of saturated solution of 9-mesityl-9,10-dihydro-9-boraanthracene in a solution of CH_2Cl_2/Pentane 1:1.

^{1}H NMR ($400\mathrm{MHz}$, $CHCl_3$-d^1) δ (ppm)$=$ 7.46 (dd, $J = 7.3$, 1.5 Hz, 2 H), 7.28-7.15 (m, 4 H), 6.86-6.77 (m, 4 H), 4.99 (s, 2 H), 2.34 (s, 3 H), 1.77 (s, 3 H), 1.48 (s, 3 H)

^{11}B NMR ($160\mathrm{MHz}$, $CHCl_3$-d^1) δ (ppm)$=$ 67.3

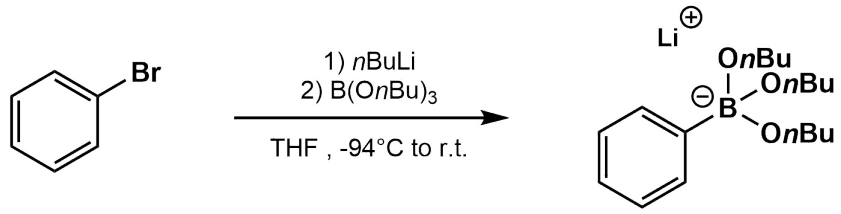
9-mesityl-9,10-dihydro-9-boraanthracene dimer (**15**) : Yield: $230\,\mathrm{mg}$, 7.9%

Crystals suitable for X-ray structure analysis have been obtained by slow evaporation of saturated solution of 9-mesityl-9,10-dihydro-9-boraanthracene dimer in a solution of CH_2Cl_2/Pentane 1:1.

^{1}H NMR ($400\mathrm{MHz}$, $CHCl_3$-d^1) δ (ppm)$=$ 7.46 (dd, $J = 7.3$, 1.5 Hz, 4 H), 7.28-7.15 (m, 8 H), 6.86-6.77 (m, 8 H), 4.99 (s, 2 H), 2.34 (s, 6 H), 1.77 (s, 6 H), 1.48 (s, 6 H)

^{11}B NMR ($160\mathrm{MHz}$, $CHCl_3$-d^1) δ (ppm)$= 67.3$

*Synthesis of lithium phenyl-tributylborate (**16**)*



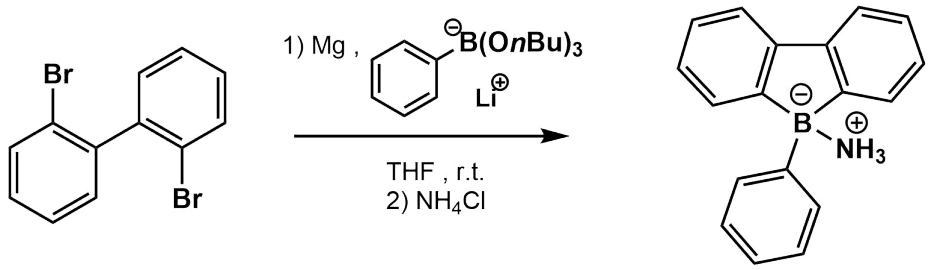
Under Ar atmosphere, at $-94\,^{\circ}\mathrm{C}$ a solution of *n*butyl lithium ($2.5\mathrm{mol\,dm^{-3}}$, $12.7\mathrm{mL}$, $31.8\mathrm{mmol}$, 1.1 equiv.) in hexane was added dropwise over a solution of bromobenzene ($3.3\mathrm{mL}$, $31.8\mathrm{mmol}$, 1.1 equiv) in THF ($20\,\mathrm{mL}$) . The reaction was stirred $1\,\mathrm{h}$ at $-94\,^{\circ}\mathrm{C}$. B(O*n*Bu)$_3$ ($7.8\mathrm{mL}$, $28.9\mathrm{mmol}$, 1 equiv.) was added dropwise at $-94\,^{\circ}\mathrm{C}$. The reaction was allowed to warm at room temperature overnight. The crude mixture was evaporated to dryness which afford the pure lithium phenyl-tributylborate as a white powder.

Yield: $7.6\mathrm{g}$, 85%

^{1}H NMR ($400\mathrm{MHz}$, MeOH-d^4) δ (ppm)$= 7.47$ (dt, $J = 15.4$, 7.7 Hz, 2 H), 7.11 (ddd, $J = 7.8$, 1.6, 0.8 Hz, 2 H), 7.06-6.95 (m, 1 H), 3.52 (t, $J = 6.7$ Hz, 6 H), 1.59-1.43 (m, 6 H), 1.43-1.29 (m, 6 H), 0.92 (t, $J = 8.7$ Hz, 9 H).

^{11}B NMR ($160\mathrm{MHz}$, MeOH-d^4) δ (ppm)$= 3.8$ (br s)

*Synthesis of 9-phenyl-9-borafluorene ammoniate (**17**)*



Under Ar atmosphere, 2,2'-dibromobiphenyl (2.00g, 6.43mmol, 1 equiv.) was mixed with phenyltributylborate (1.97g, 6.43mmol, 1 equiv.) and THF (20 mL) in a dropping funnel and added over magnesium turnings (450 g, 18.5mmol, 3 equiv.) over 30 min at constant 20 °C. The mixture was left stirring at 20 °C for 48 h. Saturated aqueous NH_4Cl (50 mL) was added. The organic phase was collected and the aqueous phase was extracted using ethyl acetate ($3 * 20$ mL). The combined organic layers were dried over $MgSO_4$ and then filtered. The solution was concentrated under reduced pressure. Precipitation into hexane following by filtration afforded 9-phenyl-9-borafluorene ammoniate as a white powder.

noindent Yield: 655 mg, 40%

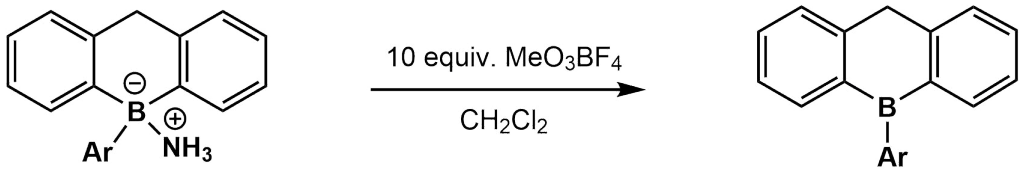
Crystals suitable for X-ray structure analysis have been obtained by slow evaporation of a saturated solution of 9-phenyl-9-borafluorene ammoniate in methanol.

^{1}H NMR (400MHz, MeOH-d^4) δ (ppm)= 7.57 (dd, J = 4.6, 3.6 Hz, 2 H), 7.51-7.46 (m, 2 H), 7.42-7.37 (m, 2 H), 7.16-6.93 (m, 7 H), 5.00 (br, 2 H).

^{13}C NMR (100MHz, acetone-d^6) δ (ppm)= 149.2, 132.0, 130.6, 126.9, 126.1, 125.7, 124.7, 118.7.

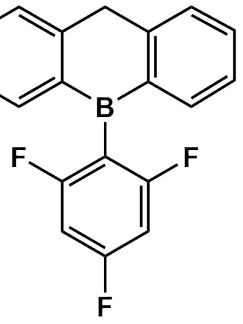
^{11}B NMR (160MHz, MeOH-d^4) δ (ppm)= -6.3 (br s)

General procedure B for synthesis of 9-aryl-9,10-dihydro-9-boraanthracene



In a glove-box, trimethyloxonium tetrafluoroborate (10 equiv.) was added over a solution of 9-aryl-9,10-dihydro-9-boraanthracene (1 equiv.) in CH_2Cl_2. The reaction was stirred for $5\,\mathrm{min}$ at room temperature. The crude mixture was filtrated over cotton. The filtrate was evaporated to dryness and diluted in a mixutre of pentane/CH_2Cl_2 10:1 and then filtered over cotton. Evaporation to dryness of the second filtrate afforded 9-aryl-9,10-dihydro-9-boraanthracene.

*Synthesis of 9-(2,4,6-trifluorophenyl)-9,10-dihydro-9-boraanthracene (**22**)*



The title compound was prepared according to the general procedure B with trimethyloxonium trifluoroborate ($105\,\mathrm{mg}$, $0.71\mathrm{mmol}$), 9-(2,4,6-trifluorophenyl)-9,10-dihydro-9-boraanthracene ammoniate ($23.2\mathrm{mg}$, $0.071\mathrm{mmol}$). 9-(2,4,6-trifluorophenyl)-9,10-dihydro-9-boraanthracene ($15.4\mathrm{mg}$, $0.050\mathrm{mmol}$, 70.0%) was isolated as an orange solid

Crystals suitable for X-ray structure analysis have been obtained by slow evaporation of a saturated solution of 9-(2,4,6-trifluorophenyl)-9,10-dihydro-9-boraanthracene dimer in a solution of CH_2Cl_2/Pentane 1:1.

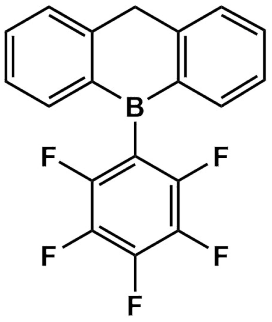
^{1}H NMR ($400\mathrm{MHz}$, $CHCl_3$-d^1) δ (ppm)= 7.78 (d, J = 7.7 Hz, 2 H), 7.65-7.67 (m, 4 H), 7.40-7.35 (m, 2 H), 6.83-6.75 (m, 2 H), 4.59 (s, 2 H)

^{13}C NMR ($100\mathrm{MHz}$, $CHCl_3$-d^1) δ (ppm)= 148.4, 138.0, 133.6, 128.2, 125.9, 125.7, 38.5

^{11}B NMR ($160\mathrm{MHz}$, $CHCl_3$-d^1) δ (ppm)= 59.9

^{19}F NMR ($377\mathrm{MHz}$, $CHCl_3$-d^1) δ (ppm)= -97.8 (s, 2F), -108.6 (s, 1F)

*Synthesis of 9-(pentafluorophenyl)-9,10-dihydro-9-boraanthracene (**23**)*



The title compound was prepared according to the general procedure B with trimethyloxonium trifluoroborate ($90\,\mathrm{mg}$, $0.61\mathrm{mmol}$), 9-(pentafluorophenyl)-9,10-dihydro-9-boraanthracene ammoniate ($20.3\mathrm{mg}$, $0.056\mathrm{mmol}$). 9-(pentafluorophenyl)-9,10-dihydro-9-boraanthracene ($12.8\mathrm{mg}$, $0.037\mathrm{mmol}$, 66.0%) was isolated as a yellow solid.

Crystals suitable for X-ray structure analysis have been obtained by slow evaporation of saturated solution of 9-(pentafluorophenyl)-9,10-dihydro-9-boraanthracene in a solution of CH_2Cl_2/Pentane 1:1.

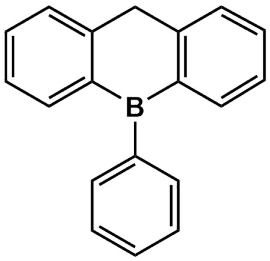
^{1}H NMR ($400\mathrm{MHz}$, $CHCl_3$-d^1) δ (ppm)= 7.72(d, J = 7.6 Hz, 2 H), 7.69-7.60 (m, 4 H), 7.42-7.37 (m, 2 H), 4.61 (s, 2 H)

^{13}C NMR ($100\mathrm{MHz}$, $CHCl_3$-d^1) δ (ppm)= 148.8, 137.8, 134.15, 129.0, 128.5, 128.4, 126.2, 38.6.

^{11}B NMR ($160\mathrm{MHz}$, $CHCl_3$-d^1) δ (ppm)= 58.5

^{19}F NMR ($377\mathrm{MHz}$, $CHCl_3$-d^1) δ (ppm)= -129.8 (br, 2 F), -153.6 (br, 1 F), -161.4 (br, 3 F)

*Synthesis of 9-phenyl-9,10-dihydro-9-boraanthracene (**24**)*



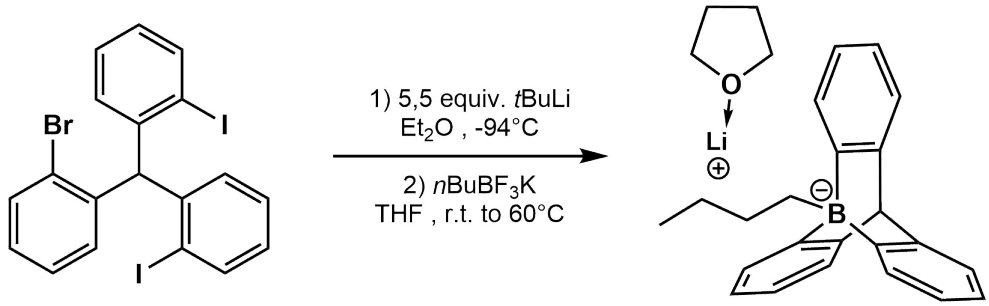
The title compound was prepared according to the general procedure B with trimethyloxonium trifluoroborate ($100\,\mathrm{mg}$, $0.67\mathrm{mmol}$), 9-phenyl-9,10-dihydro-9-boraanthracene ammoniate ($17.5\mathrm{mg}$, $0.065\mathrm{mmol}$). 9-phenyl-9,10-dihydro-9-boraanthracene ($11.6\mathrm{mg}$, $0.046\mathrm{mmol}$, 71.0%) was isolated as a white solid.

^{1}H NMR ($400\mathrm{MHz}$, $CHCl_3$-d^1) δ (ppm)$=$ 7.61(d, $J = 7.8$ Hz, 2 H), 7.65-7.56 (m, 6 H), 7.53-7.47 (m, 2 H), 7.37-7.32 (m, 2 H), 4.57 (s, 2 H)

^{13}C NMR ($100\mathrm{MHz}$, $CHCl_3$-d^1) δ (ppm)$=$ 148.4, 138.7, 132.6, 128.1, 127.4, 125.7, 38.6

^{11}B NMR ($160\mathrm{MHz}$, $CHCl_3$-d^1) δ (ppm)$=$ 61.1

*Synthesis of 9-nbutyl-9-boratriptycene lithium/THF complex (**28**)*



Under Ar atmosphere, at $-94\,^{\circ}\mathrm{C}$, a solution of *t*butyl lithium ($1.9\mathrm{mol\,dm^{-3}}$, $5.0\mathrm{mL}$, $9.56\mathrm{mmol}$, 5.5 equiv.) in pentane was added dropwise over a solution of 2,2'-diiodo-2"-bromotriphenylmethane ($1.00\mathrm{g}$, $1.74\mathrm{mmol}$, 1 equiv.) in Et_2O ($30\,\mathrm{mL}$). The reaction was stirred $3\,\mathrm{h}$ at $-94\,^{\circ}\mathrm{C}$. Potassium*n*butyltrifluoroborate ($284\,\mathrm{mg}$, $1{,}73\,\mathrm{mmol}$, 1 equiv.) was added as a solid at $-94\,^{\circ}\mathrm{C}$ under a vigorous flow or Ar. The reaction was stirred at $-94\,^{\circ}\mathrm{C}$ for $1\,\mathrm{h}$ then allowed to warm at room temperature and THF ($30\,\mathrm{mL}$) was added. The reaction was warm at $60\,^{\circ}\mathrm{C}$ for $10\,\mathrm{min}$ under an Ar flux and then refluxed for $48\,\mathrm{h}$. The crude mixture was concentrated under reduced pressure, redilute in DCM and then filtered. The filtrate was evaporated and dried over hard vacuum for $48\,\mathrm{h}$ affording 9-*n*butyl-9-boraanthracene lithium/THF complex.

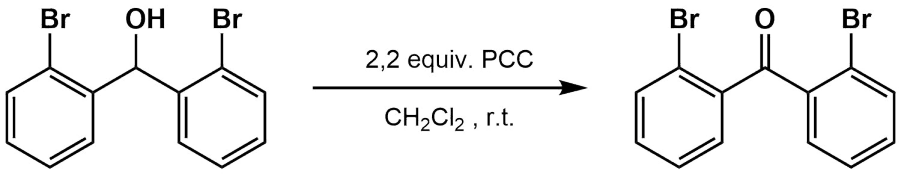
Due to the highly hygroscopic character of the compound, no yield have been obtained. The compound is used without any further purification to perform the cation methathesis.

Isolated with 90% purity.

^{1}H NMR ($400\mathrm{MHz}$, MeOH-d^4) δ (ppm)$=$ 7.36 (d, $J = 6.6$ Hz, 3 H), 7.08 (m, 3 H), 6.68-6.59 (m, 6 H), 5.16 (s, 1 H, Ar_3CH), 3.69 (m, 4 H), 1.98 (m, 2 H), 1.83 (m, 4 H), 1.65 (m, 2 H), 1.34 (m, 2 H), 1.09 (m, 3 H)

^{11}B NMR ($160\mathrm{MHz}$, MeOH-d^4) δ (ppm)$=$ -13.98 (br s)

*Synthesis of 2,2'-dibromobenzophenone (**30**)*



Prepared accordind to a litterature procedure [3]. Pyridinium chlorochromate ($13.4\mathrm{g}$, $61.4\mathrm{mmol}$, 2.5 equiv.) was added to a solution of bis(2-bromophenyl)methanol ($7.50\mathrm{g}$, $24.5\mathrm{mmol}$, 1 equiv.) in CH_2Cl_2 ($60\,\mathrm{mL}$). The reaction was stirred overnight at room temperature. The reaction mixture was extracted with ethyl acetate and filtered over a pad of Celite. The filtrate was evaporated and purification by silica gel chromatography with a solution of cyclohexane/ethyl acetate 95:5 afforded 2,2'-dibromobenzophenone as white crystals. ^{1}H and ^{13}C NMR data are in good aggreament with the one reported in the literature.

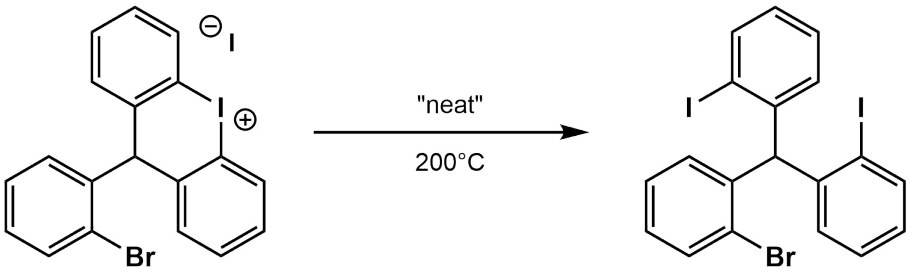
Yield: $6.86\mathrm{g}$, 86.3%

Crystals suitable for X-ray structure analysis have been obtained by slow evaporation of a saturated solution of 2,2'-dibromobenzophenone in a solution of Et_2O/Pentane 1:1.

^{1}H NMR ($400\mathrm{MHz}$, $CHCl_3$-d^1) δ (ppm)= 7.66-7.63 (m, 2 H), 7.47-7.44(m, 2 H), 7.40-7.33(m, 4 H)

^{13}C NMR ($100\mathrm{MHz}$, $CHCl_3$-d^1) δ (ppm)= 195.4, 139.3, 134.1, 132.5, 131.3, 127.3, 121.2

*Synthesis of 2,2'-diiodo-2"-bromotriphenylmethane (**32**)*



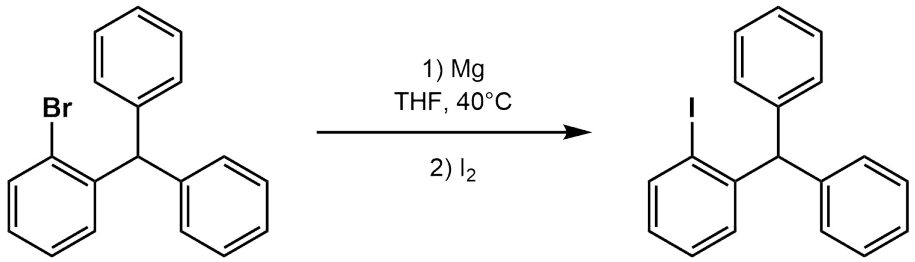
Prepared according to a literature procedure [4]. Under Ar atmosphere, 10-(2-bromophenyl)-10*H*-dibenzoiodonium iodide ($8.80\mathrm{g}$, $15.3\mathrm{mmol}$, 1 equiv.) was warmed at $200\,^{\circ}\mathrm{C}$ for $15\,\mathrm{min}$ in a sealed schlenk. The reaction was allowed to cool down at room temperature. The crude was diluted using CH_2Cl_2 and washed using saturated sodium thiosulfate ($200\,\mathrm{mL}$), H_2O ($200\,\mathrm{mL}$) and then brine ($200\,\mathrm{mL}$). The organic phase was dried over $MgSO_4$ and then filtered and concentrated to dryness under reduced pressure. Recrystalisation from methanol afforded pure 2,2'-diiodo-2"-bromotriphenylmethane as off-white powder. ^{1}H and ^{13}C NMR data are in good agreement with the one reported in the literature.

Yield: $6.24\mathrm{g}$, 71%

^{1}H NMR ($400\mathrm{MHz}$, $CHCl_3$-d^1) δ (ppm)$=$ 7.93 (d, $J = 8.0$ Hz, 2 H), 7.64 (d, $J = 8.0$ Hz, 1 H), 7.30-7.16 (m, 4 H), 7.00 (t, $J = 8.0$ Hz, 2 H), 6.72 (d, $J = 8.0$ Hz, 3 H), 6.04 (s, 1 H, Ar_3CH)

^{13}C NMR ($100\mathrm{MHz}$, $CHCl_3$-d^1) δ (ppm)$=$ 144.1, 141.1, 140.2, 133.3, 131.1, 130.7, 128.6, 128.5, 127.3, 126.7, 103.6, 65.4 (Ar_3CH)

Synthesis of 2-iodotriphenylmethane ***33***



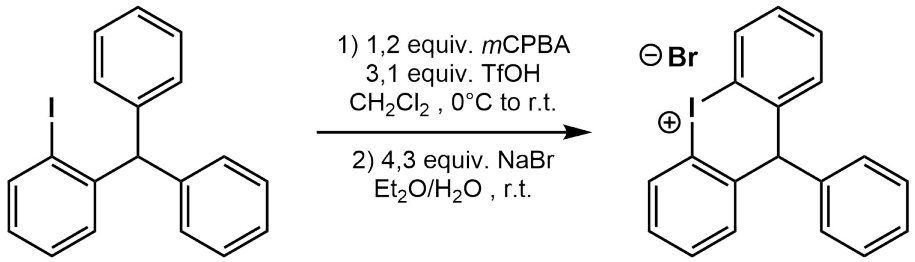
Under Ar atmosphere, a solution of 2-bromotriphenylmethane ($46.3\mathrm{g}$, $143\,\mathrm{mmol}$, 1 equiv.) in THF ($150\,\mathrm{mL}$) was added dropwise over magnesium turnings over $1.5\mathrm{h}$. The reaction was stirred at $40\,^{\circ}\mathrm{C}$ for $2\,\mathrm{h}$ then allowed to cool down at room temperature. At $0\,^{\circ}\mathrm{C}$, I_2 ($40.0\mathrm{g}$, $158\,\mathrm{mmol}$, 1.1 equiv.) was added portionwise. The reaction was stirred for $30\,\mathrm{min}$ at $0\,^{\circ}\mathrm{C}$. Saturated aqueous sodium thiosulfate ($200\,\mathrm{mL}$) is added. The organic phase is collected and the aqueous phase is extracted using Et_2O ($3 * 100\,\mathrm{mL}$). The combined organic layers were dried over $MgSO_4$ and then filtered. Concentration to dryness under reduced pressure afforded pure 2-iodotriphenylmethane as pale yellow crystals.

Yield: $47.3\mathrm{g}$, 93.0%

^{1}H NMR ($400\mathrm{MHz}$, $CHCl_3$-d^1) δ (ppm)= 7.87 (d, $J = 8.0, 1.3$ Hz, 1 H), 7.32-7.21(m, 8 H), 7.08-7.05 (m, 5 H), 6.94 (d, $J = 8.0, 1.3$ Hz, 1 H), 5.83 (s, 1 H, Ar_3CH).

^{13}C NMR ($100\mathrm{MHz}$, $CHCl_3$-d^1) δ (ppm)= 146.4, 142.8, 140.0, 131.0, 129.9, 129.5, 128.5, 128.3, 128.1, 126.6, 60.9 (Ar_3CH)

*Synthesis of 10-phenyl-10H-dibenzoiodonium Bromide (**34**)*



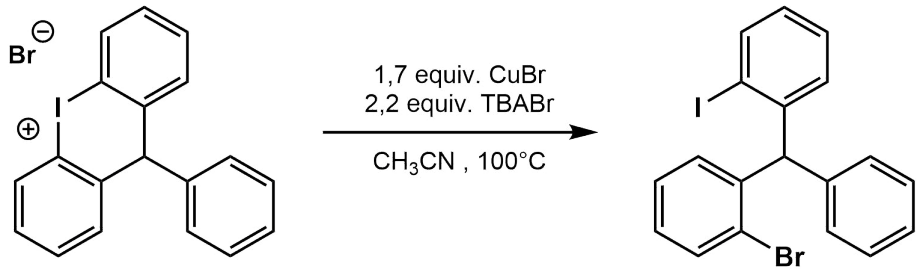
Prepared according to the literature procedure [4]. Under Ar atmosphere, at $0\,^{\circ}\mathrm{C}$, 2-iodotriphenylmethane ($47.3\mathrm{g}$, $127\,\mathrm{mmol}$, 1 equiv.) was added portionwise over a solution of 3-chloroperbenzoic acid (70-75% $38.0\mathrm{g}$, $153\,\mathrm{mmol}$, 1.2 equiv) over $10\,\mathrm{min}$. The reaction was stirred at $0\,^{\circ}\mathrm{C}$ for $10\,\mathrm{min}$. Trifluoromethanesulfonic acid ($36.0\mathrm{mL}$, $395\,\mathrm{mmol}$, 3.1 equiv.) was added via a glass syringe over $10\,\mathrm{min}$. The reaction was stirred at $0\,^{\circ}\mathrm{C}$ for $20\,\mathrm{min}$ and allowed to warm at room temperature for $2\,\mathrm{h}$. The crude mixture was concentrated to dryness under reduced pressure. The resulting solid was suspended in Et_2O ($800\,\mathrm{mL}$) and H_2O ($800\,\mathrm{mL}$) and solid sodium bromide ($65.5\mathrm{g}$, $637\,\mathrm{mmol}$, 5 equiv.) was added. The mixture ws shaken vigorously for $5\,\mathrm{min}$. Filtration and repeated washes using Et_2O and H_2O afforded pure 10-phenyl-10*H*-dibenzoiodonium bromide as a pale yellow powder. ^{1}H and ^{13}C NMR data are in good agreement with the one reported in the literature.

Yield: $52.3\mathrm{g}$, 91.1%

^{1}H NMR ($400\mathrm{MHz}$, DMSO-d^6) δ (ppm)$=$ 8.27 (dd, $J = 8.0$, 1.0 Hz, 2 H), 7.68 (td, $J = 8.0$, 1.0 Hz, 2 H), 7.46 (td, $J = 8.0$, 1.0 hertz, 1 H), 7.27 (m, 3 H), 6.78 (d, $J = 8.0$ Hz, 2 H), 6.09 (s, 1 H, Ar_3CH).

^{13}C NMR ($100\mathrm{MHz}$, DMSO-d^6) δ (ppm)$=$ 140.3, 138.3, $135.$, 132.7, 131.7, 129.6, 128.9, 127.9, 127.4, 117.4, 55.9 (Ar_3CH)

*Synthesis of 2-iodo-2'-bromotriphenylmethane (**35**)*



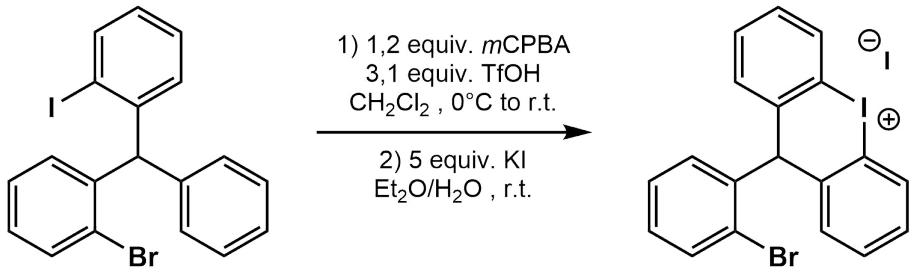
Prepared according to a literature procedure [4]. Under Ar atmosphere, 10-phenyl-10*H*- dibenzoiodonium Bromide ($52.3\mathrm{g}$, $116\,\mathrm{mmol}$, 1 equiv.) was added to a solution of copper bromide ($26.0\mathrm{g}$, $181\,\mathrm{mmol}$, 1.5 equiv.) and tetrabutylammonium bromide ($90.0\mathrm{g}$, $116\,\mathrm{mmol}$, 2.4 equiv.) in dried and degased acetonitrile. The reaction was refluxed for 7 days. The crude was concentrated to dryness under reduced pressure and redilute into toluene and then filtered over a plug of silica gel. The filtrate was concentrated to dryness. Recrystalisation from methanol afforded pure 2-iodo-2'-bromotriphenylmethane as off-white powder. ^{1}H and ^{13}C NMR data are in good agreement with the one reported in the literature.

Yield: $35{,}5\,\mathrm{g}$, 68%

^{1}H NMR ($400\mathrm{MHz}$, $CHCl_3$-d^1) δ (ppm)= 7.90 (dd, $J = 8.0$, 1.0 Hz, 1 H), 7.60 (dd, $J = 8.0$, 1.0 Hz, 1 H), 7.34-7.18 (m, 5 H), 7.13 (td, $J = 8.0$, 1.0 Hz, 1 H), 7.03 (dd, $J = 8.0$, 1.0 Hz, 2 H), 6.95 (td, $J = 8.0$, 1.0 Hz, 1 H), 6.79 (dd, $J = 8.0$, 1.0 Hz, 2 H), 6.02 (s, 1 H, Ar_3CH).

^{13}C NMR ($100\mathrm{MHz}$, $CHCl_3$-d^1) δ (ppm)= 145.2, 142.2, 141.1 , 140.1, 133.1, 131.2, 130.7, 130.0, 128.5, 128.3, 128.2, 128.0, 127.2, 126.7, 126.3, 102.9, 60.8 (Ar_3CH)

*Synthesis of 10-(2-bromophenyl)-10H-dibenzoiodonium iodide (**36**)*



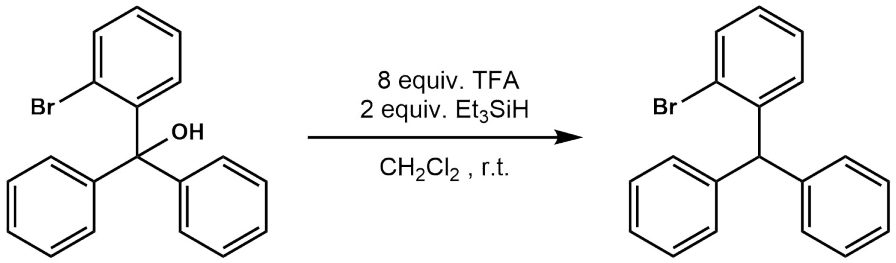
Prepared according to the literature procedure [4]. Under Ar atmosphere, at $0\,^{\circ}\mathrm{C}$, 2-iodo-2'-bromotriphenylmethane ($35.5\mathrm{g}$, $78.8\mathrm{mmol}$, 1 equiv.) was added portionwise over a solution of 3-chloroperbenzoic acid (70-75%, $23.3\mathrm{g}$, $94.7\mathrm{mmol}$, 1.2 equiv.) in CH_2Cl_2 ($150\,\mathrm{mL}$) over $10\,\mathrm{min}$. The reaction was stirred at $0\,^{\circ}\mathrm{C}$ for $10\,\mathrm{min}$. Trifluoromethanesulfonic acid ($22.0\mathrm{mL}$, $245\,\mathrm{mmol}$, 3.1 equiv.) was added via a glass syringe over $10\,\mathrm{min}$. The reaction was stirred at $0\,^{\circ}\mathrm{C}$ for $20\,\mathrm{min}$ and allowed to warm at room temperature for $2\,\mathrm{h}$. The crude mixture was concentrated to dryness under reduced pressure. The resulting solid was suspended in Et_2O ($800\,\mathrm{mL}$) and H_2O ($800\,\mathrm{mL}$) and solid sodium bromide ($65.0\mathrm{g}$, $394\,\mathrm{mmol}$, 5 equiv.) was added. The mixture was shaken vigorously for $5\,\mathrm{min}$. Filtration and repeated washes using Et_2O and H_2O afforded pure 10-(2-bromophenyl)-10*H*-dibenzoiodonium iodide as a yellow powder. ^{1}H and ^{13}C NMR data are in good agreement with the one reported in the literature.

Yield: $40.7\mathrm{g}$, 90%

^{1}H NMR ($400\mathrm{MHz}$, DMSO-d^6) δ (ppm)$=$ 8.20 (dd, $J = 8.0$, 1.0 Hz, 2 H), 7.83 (dd, $J = 8/0$, 1.0 Hz, 2 H), 7.72 (dd, $J = 8.0$, 1.0 Hz, 1 H), 7.60 (td, $J = 8.0$, 1.0 Hz, 2 H), 7.47-7.39 (m, 3 H), 7.33 (td, $J = 8.0$, 1.0 Hz, 1 H), 7.23 (dd, $J = 8.0$, 1.0 Hz, 1 H), 6.02 (s, 1 H, Ar_3CH).

^{13}C NMR ($100\mathrm{MHz}$, DMSO-d^6) δ (ppm)$=$ 138.9, 135.4, 135.1, 135.0, 133.4, 132.8, 131.7, 130.7, 130.0, 128.0, 117.2, 110.0, 58.8 (Ar_3CH)

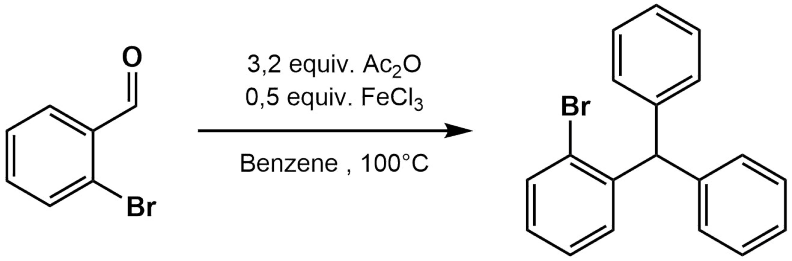
*Synthesis of 2-bromotriphenylmethane (**37**)*



Trifluoroacetic acid (9.50mL, 122 mmol, 8 equiv.) was added dropwise to a solution of 2-bromotriphenylmethanol (5.16g, 15,2 mmol, 1 equiv.) in DCM (50 mL at 0 °C. The mixture was stirred at 0 °C for 5 min. At the same temperature, triethylsilane (3.47mL, 30 mmol, 2 equiv.) was added dropwise. The mixture was allowed to warm at room temperature and stirred overnight. The crude mixture was concentrated under reduced pressure. Purification by silica gel chromatography using a solution of hexane/toluene 80:20 as solvent afforded 2-bromotriphenylmethane as white crystals. ^{1}H and ^{13}C NMR data are in good agreement with the one reported in the literature [5].

Yield: 3.74g, 76.0%

Optimal synthesis :



Prepared according to a modified literature procedure [6]. Under Ar atmosphere, $FeCl_3$ (1.43g, 8.63mmol, 0.5 equiv.) was added over a solution of 2-bromobenzaldehyde (2.0mL, 17.1mmol, 1 equiv.) in acetic anhydride (5.2mL, 54.7mmol, 3.2 equiv.) and benzene (23 mL). The reaction was refluxed overnight. The crude mixture is concentrated under reduced pressure and filtrated through a silica gel plug. The filtrate is concentrated under reduced pressure. Purification by silica gel chromatography using a solution of hexane/toluene 80:20 as solvent afforded 2-bromophenylmethane as white cristals.

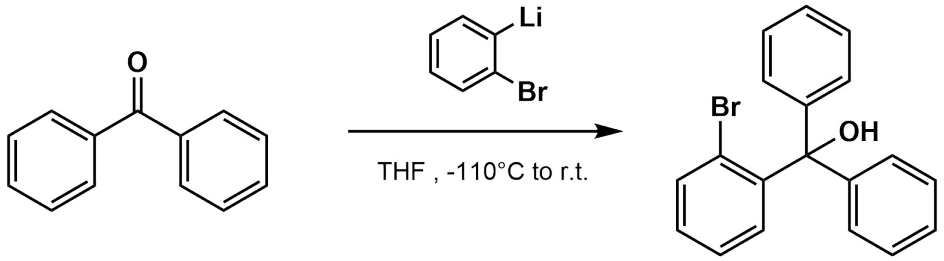
Yield: 2.41g, 44.0%

^{1}H NMR (400MHz, $CHCl_3$-d^1) δ (ppm)= 7.57 (d, J = 8.4 Hz, 1 H), 7.31-7.18(m, 7 H), 7.10-7.06 (m, 5 H), 6.94 (d, J = 7.6 Hz, 1 H), 5.95 (s, 1H, Ar_3CH).

^{13}C NMR (100MHz, $CHCl_3$-d^1) δ (ppm)= 143.2, 142.6, 133.1 , 131.4, 129.6, 128.3, 128.0, 127.18,

126.5, 125.5, 55.9 (Ar_3CH)

*Synthesis of 2-bromotriphenylmethanol (**38**)*



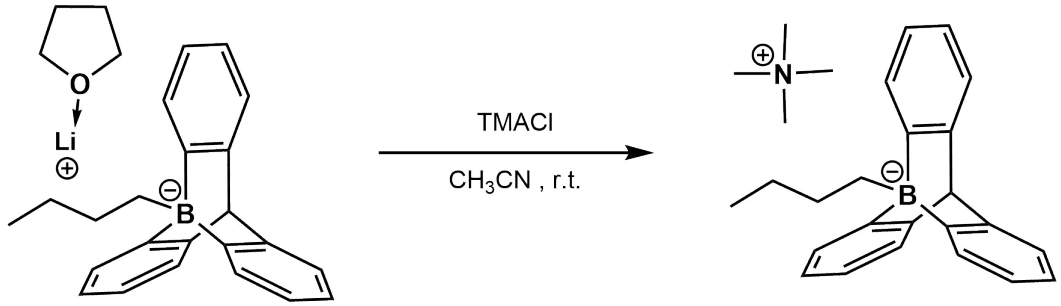
Prepared accordind to a litterature procedure [7]. Under Ar atmosphere, at $-110\,^{\circ}\mathrm{C}$, a solution of *n*butyl lithium ($2.5\mathrm{mol\,dm^{-3}}$, $25{,}8\,\mathrm{mL}$, $64.5\mathrm{mmol}$, 1 equiv.) in hexane was added dropwise to a solution of 1,2-dobromobenzene ($15.2\mathrm{g}$, $64.5\mathrm{mmol}$, 1 equiv.) in THF ($100\,\mathrm{mL}$). The reaction was stirred $1.5\mathrm{h}$ at $-110\,^{\circ}\mathrm{C}$. A solution of benzophenone ($11{,}7\,\mathrm{g}$, $64{,}4\,\mathrm{mmol}$, 1 equiv.) in THF ($40\,\mathrm{mL}$) was added dropwise. The reaction was stirred $2\,\mathrm{h}$ at $-110\,^{\circ}\mathrm{C}$ then allowed to warm at room temperature overnight. H_2O ($100\,\mathrm{mL}$) is added. The organic phase is collected and the aqueous phase was extracted using Et_2O ($3 * 50\,\mathrm{mL}$. The combined organic layers were dried over $MgSO_4$ and then filtered. Purification by silica gel chromatography using a solution of hexane/toluene 80:20 as solvent afforded 2-bromotriphenylmethanol as white crystals. ^{1}H and ^{13}C NMR data are in good agreement with the one reported in the literature.

Yield: $5.16\mathrm{g}$, 23.6%

^{1}H NMR ($400\mathrm{MHz}$, $CHCl_3$-d^1) δ (ppm)= 7.38 (dd, $J = 8.3$, 1.5 Hz, 2 H), 7.34-7.18(m, 12 H)

^{13}C NMR ($100\mathrm{MHz}$, $CHCl_3$-d^1) δ (ppm)= 145.5, 145.0 , 134.8, 131.9, 129.2, 127.9, 127.3, 126.8, 122.9, 83.1

*Synthesis of tetramethylammonium 9-nbutyl-9-boratriptycene (**43**)*



Equivalent calculated from 2,2'-diiodo-2"-bromotriphenylmethane. Tetramethylammonium chloride (210 mg, 1.91mmol, 1.1 equiv.) was added as a solid in a solution of 9-*n*butyl-9-boraanthracene lithium/THF complex (1 equiv.) in acetonitrile (50 mL). The reaction was stirred overnight at room temperature. The reaction mixture was filtered. The filtrate was left in the fridge for 3 h and then filtrated again. The second filtrate was concentrated to dryness under reduced pressure. Precipitation in a solution of pentane/ethyl acetate 50:50 afforded pure tetramethylammonium 9-*n*butyl-9-boratriptycene as white powder.

Yield: 150 mg, 22.4%

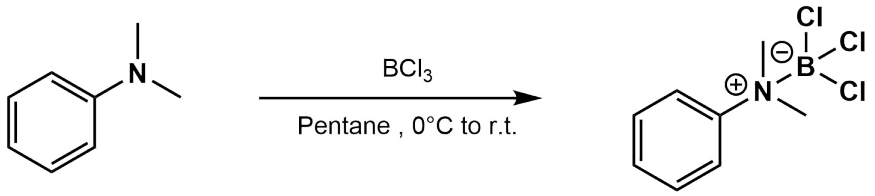
Crystals suitable for X-ray structure analysis were obtained by a vapour gas diffusion of Et_2O in a saturated solution of tetramethylammonium 9-*n*butyl-9-boratriptycene in acetonitrile for three weeks.

^{1}H NMR (400MHz, MeCN-d^3) δ (ppm)= 7.27 (d, J = 6.6 Hz, 3 H), 7.07 (m, 3H), 6.68-6.59 (m, 6 H), 5.13 (s, 1 H, Ar_3CH), 2.87 (m, 12 H), 1.91 (m, 2 H), 1.62 (m, 2 H), 1.24 (m, 2 H), 1.07 (m, 3 H)

^{13}C NMR (100MHz, MeCN-d^3) δ (ppm)= 150.7, 128.1, 122.2, 122.1, 120.7, 55.9, 14.2

^{11}B NMR (160MHz, MeCN-d^3) δ (ppm)= -14.02 (br s)

*Synthesis of N,N-dimethylaniline boron trichloride (**45**)*



Prepared according to a modified literature procedure [8]. Under Ar atmosphere, at $0\,^{\circ}\mathrm{C}$, a solution of boron trichloride ($1.0\mathrm{mol\,dm^{-3}}$, $15.0\mathrm{mL}$, $15.0\mathrm{mmol}$, 1 equiv. equiv.) in pentane was added to a solution of *N,N*-dimethylaniline (($3.0\mathrm{mL}$, $23.7\mathrm{mmol}$, 1.5 equiv.) in pentane ($15\,\mathrm{mL}$). The reaction was stirred at $0\,^{\circ}\mathrm{C}$ for $1\,\mathrm{h}$. The solvent was removed via cannula filtration and the solid material was washed using pentane ($2 * 15\,\mathrm{mL}$). Evaporation to dryness afforded pure *N,N*-dimethylaniline boron trichloride as a white powder.

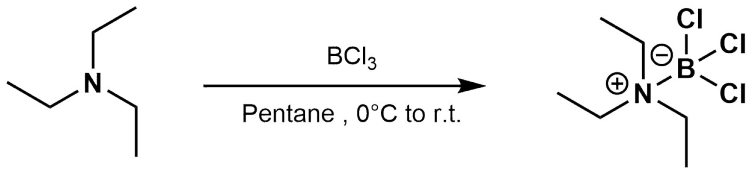
Yield: $3.54\mathrm{mg}$, 99%

^{1}H NMR ($400\mathrm{MHz}$, $CHCl_3$-d^1) δ (ppm)= 7.64 (d, $J = 8.2$ Hz, 2 H), 7.42 (m, 3 H), 3.52 (m, 6 H)

^{13}C NMR ($100\mathrm{MHz}$, $CHCl_3$-d^1) δ (ppm)= 145.1, 128.6, 128.5, 50.3

^{11}B NMR ($160\mathrm{MHz}$, $CHCl_3$-d^1) δ (ppm)= 9.34 (br s)

*Synthesis of triethylamine boron trichloride (**46**)*



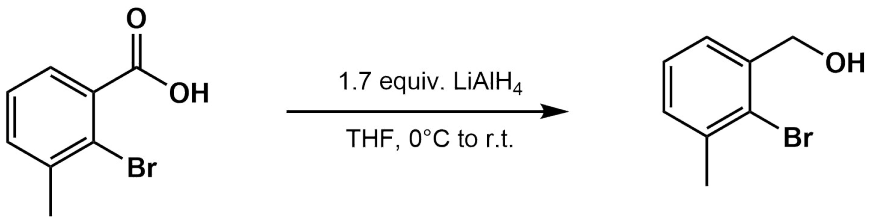
Prepared according to modified literature procedure [8]. Under Ar atmosphere, at $0\,^{\circ}\mathrm{C}$, a solution of boron trichloride ($1.0\mathrm{mol\,dm^{-3}}$, $7.0\mathrm{mL}$, $7.0\mathrm{mmol}$, 1 equiv. equiv.) in pentane was added to a solution of triethylamine ($1.0\mathrm{mL}$, $7.2\mathrm{mmol}$, 1 equiv.) in pentane ($10\,\mathrm{mL}$). The reaction was stirred at $0\,^{\circ}\mathrm{C}$ for $1\,\mathrm{h}$. The solvent was removed via cannula filtration and the solid material was washed using pentane ($2 * 15\,\mathrm{mL}$). Evaporation to dryness afforded pure triethylamine boron trichloride as a white powder.

Yield: $1.51\mathrm{g}$, 99%

^{1}H NMR ($400\mathrm{MHz}$, $CHCl_3$-d^1) δ (ppm)= 3.39-3.30 (m, 6 H) 1.30 (t, $J = 7.4$ Hz, 9 H)

^{11}B NMR ($160\mathrm{MHz}$, $CHCl_3$-d^1) δ (ppm)= 8.3 (br s)

*Synthesis of 2-bromo-3-methyl-benzenemethanol (**48**)*



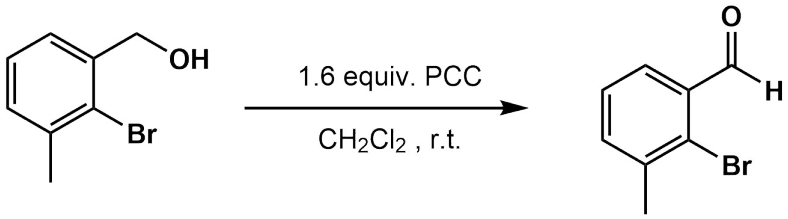
At $0\,^{\circ}\mathrm{C}$, a solution of 2-bromo-3-methyl-benzoic acid ($15.4\mathrm{g}$, $71.6\mathrm{mmol}$, 1 equiv.) in THF ($30\,\mathrm{mL}$) was added dropwise to a solution of $LiAlH_4$ ($4.65\mathrm{g}$, $122\,\mathrm{mmol}$, 1.7 equiv.) in THF ($150\,\mathrm{mL}$). The mixture was stirred at room temperature overnight. An aqueous solution of KOH ($1.0\mathrm{mol\,dm^{-3}}$, $200\,\mathrm{mL}$) was added slowly. The reaction mixture was diluted with H_2O ($100\,\mathrm{mL}$). The organic phase was collected and the aqueous phase was extracted using Et_2O ($3 * 100\,\mathrm{mL}$). The combined organic layers were dried over $MgSO_4$ and then filtrated. Concentration to dryness under reduced pressure afforded pure 2-bromo-3-methyl-benzenemethanol as white crystals. ^{1}H and ^{13}C NMR data are in good agreement with the one reported in the literature [9].

Yield: $14.3\mathrm{g}$, 99%

^{1}H NMR ($400\mathrm{MHz}$, $CHCl_3$-d^1) δ (ppm)= 7.31-7.29 (m, 1 H), 7.23 (br t, $J = 7.6$ Hz, 1 H), 7.19 (dd, $J = 7.6$, 1.6 Hz, 1 H), 4.76 (d, $J = 8.0$ Hz, 1 H), 2.43 (s, 3 H), 2.09 (t, $J = 6.4$ Hz, 1 H)

^{13}C NMR ($100\mathrm{MHz}$, $CHCl_3$-d^1) δ (ppm)= 140.2, 138.6, 130.2, 127.3, 126.5, 125.3, 65.9, 23.5.

*Synthesis of 2-bromo-3-methyl-benzaldehyde (**49**)*



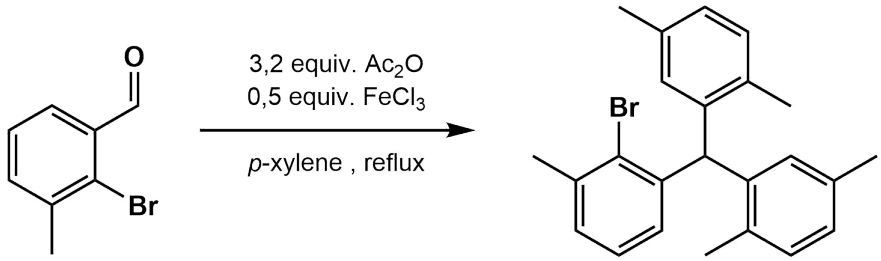
Pyridinium chlorochromate ($27.2\mathrm{g}$, $126\,\mathrm{mmol}$, 1.6 equiv.) was added to a solution of 2-bromo-3-methyl-benzenemethanol ($16.1\mathrm{g}$, $80.0\mathrm{mmol}$, 1 equiv.) in DCM ($150\,\mathrm{mL}$). The reaction was stirred overnight at room temperature. The reaction mixture was extracted with ethyl acetate and filtered over a pad of Celite. The filtrate was evaporated and purification by silica gel chromatography with a solution of hexane/toluene 80:20 afforded pure 2-bromo-3-methyl-benzaldehyde as white crystals. ^{1}H and ^{13}C NMR data are in good agreement with the one reported in the literature [9].

Yield: $7.97\mathrm{g}$, 50%

^{1}H NMR ($400\,\mathrm{MHz}$, $CHCl_3$-d^1) δ (ppm)= 10.45 (d, $J = 0.8$ Hz, 1 H), 7.75-7.73 (m, 1 H), 7.48 (ddd, $J = 7.6, 1.6, 0.8$ Hz, 1 H) 7.32 (br t, $J = 7.6$ Hz, 1 H), 2.43 (s, 3 H).

^{13}C NMR ($100\mathrm{MHz}$, $CHCl_3$-d^1) δ (ppm)= $192.8, 139.7, 136.4, 134.1, 129.7, 127.5, 127.45, 23.0$.

*Synthesis of (2-bromo-3-methyl-phenyl)-dip-xylylmethane (**50**)*



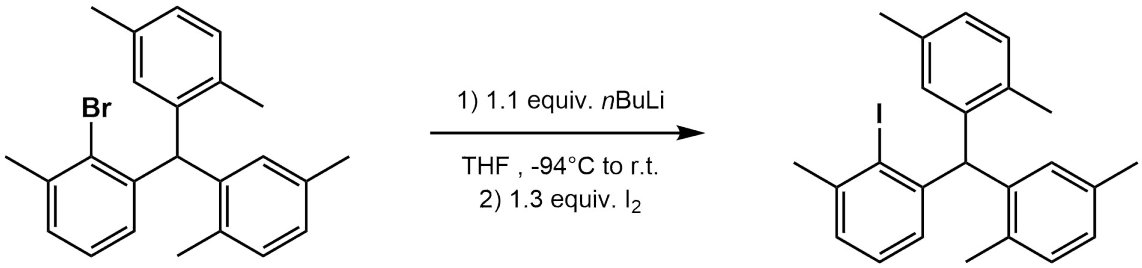
Prepared according to a modified literature procedure [6]. Under Ar atmosphere, $FeCl_3$ (3.10g, 19.1mmol, 0.5 equiv.) was added over a solution of 2-bromo-3-methyl-benzaldehyde (8.00g, 40.2mmol, 1 equiv.) in acetic anhydride (12.0mL, 127 mmol, 3.2 equiv.) and *p*-xylene (70 mL). The reaction was refluxed overnight. The crude mixture was concentrated under reduced pressure and filtrated through a plug of silica gel. The filtrate was concentrated under reduced pressure. Purification by silica gel chromatography using a solution of hexane/toluene 80:20 as solvent afforded pure (2-bromo-3-methyl-phenyl)-di*p*-xylylmethane as white cristals.

Yield: 12.8g, 81.0%

^{1}H NMR (400MHz, $CHCl_3$-d^1) δ (ppm)= 7.13-7.3 (m, 4 H), 6.95 (dd, J = 7.6, 1.4 Hz, 2 H), 6.65 (dd, J = 7.5, 1.9 Hz, 1 H), 6.48 (d, J = 1.1 Hz, 2 H), 5.95 (s, 1 H), 2.42 (s, 3 H), 2.19 (s, 3 H), 2.11 (s, 3 H).

^{13}C NMR (100MHz, $CHCl_3$-d^1) δ (ppm)= 142.9, 140.8, 138.7, 135.0, 133.9, 130.2, 129.7, 128.9, 128.8, 128.6, 127.2, 126.5, 50.8, 24.3, 21.4, 19.2 .

*Synthesis of (2-iodo-3-methyl-phenyl)-dip-xylylmethane (**51**)*



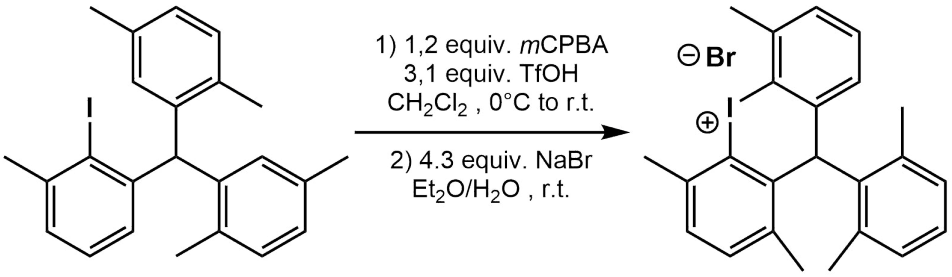
Under Ar atmosphere, at $-94\,^{\circ}\mathrm{C}$, a solution of *n*butyl lithium ($2.5\mathrm{mol\,dm^{-3}}$, $14.9\mathrm{mL}$, $37.1\mathrm{mmol}$, 1.1 equiv.) in hexane is added dropwise to a solution of (2-bromo-3-methyl-phenyl)-di*p*-xylylmethane ($13.3\mathrm{g}$, $33.8\mathrm{mmol}$, 1 equiv.) in THF ($100\,\mathrm{mL}$). The reaction was stirred at $-94\,^{\circ}\mathrm{C}$ for $1\,\mathrm{h}$ then allowed to warm at room temperature for $2\,\mathrm{h}$. I_2 ($11.2\mathrm{g}$, $43.9\mathrm{mmol}$, 1.3 equiv.) was added as a solid portion-wise. The reaction was stirred $1\,\mathrm{h}$ at room temperature. Saturated aqueous solution of thiosulfate ($150\,\mathrm{mL}$) was added. The organic phase was collected and the aqueous phase was extracted using Et_2O ($3 * 100\,\mathrm{mL}$). The combined orgainic layers were dried over $MgSO_4$ and then filtrated. Concentration to dryness under reduced pressure afforded pure (2-bromo-3-methyl-phenyl)-di*p*-xylylmethane as white cristals.

Yield: $14.1\mathrm{g}$, 95.0%

^{1}H NMR ($400\mathrm{MHz}$, $CHCl_3$-d^1) δ (ppm)= 7.13-7.3 (m, 4 H), 6.97 (d, $J = 7.6$ Hz, 2 H), 6.61 (dd, $J = 6.9, 2.5$ Hz, 1 H), 6.46 (d, $J = 1.1$ Hz, 2 H), 5.82 (s, 1 H), 2.50 (s, 3 H), 2.20 (s, 3 H), 2.12 (s, 3 H).

^{13}C NMR ($100\mathrm{MHz}$, $CHCl_3$-d^1) δ (ppm)= 146.3, 142.6, 135.1, 134.8, 130.2, 130.0, 129.8, 128.9, 128.3, 127.9, 127.5, 127.19, 127.0 56.4, 30.4, 21.4, 19.4 .

*Synthesis of 10-(3-methyl-phenyl)-10H-dip-xyloiodonium Bromide (**52**)*



Prepared according to a modified literature procedure [4]. Under Ar atmosphere, at $0\,^{\circ}\mathrm{C}$, (2-iodo-3-methyl-phenyl)-di*p*-xylylmethane ($17.1\mathrm{g}$, $39.9\mathrm{mmol}$, 1 equiv.) was added portionwise over a solution of 3-chloroperbenzoic acid (70-75% $8.05\mathrm{g}$, $46.7\mathrm{mmol}$, 1.2 equiv.) over $10\,\mathrm{min}$. The reaction was stirred at $0\,^{\circ}\mathrm{C}$ for $10\,\mathrm{min}$. Trifluoromethanesulfonic acid ($10.7\mathrm{mL}$, $120.6\mathrm{mmol}$, 3.1 equiv.) was added via a glass syringe over $10\,\mathrm{min}$. The reaction was stirred at $0\,^{\circ}\mathrm{C}$ for $20\,\mathrm{min}$ and allowed to warm at room temperature for $3\,\mathrm{h}$. The crude mixture was concentrated to dryness under reduced pressure. The resulting solid was suspended in acetone ($300\,\mathrm{mL}$) and H_2O ($800\,\mathrm{mL}$) and solid sodium bromide ($17.5\mathrm{g}$, $170\,\mathrm{mmol}$, 4.3 equiv.) was added. The mixture was shaken vigorously for $5\,\mathrm{min}$. Filtration and repeated washes using acetone and H_2O afforded pure 10-(3-methyl-phenyl)-10*H*-di*p*-xyloiodonium bromide as a pale yellow powder.

Yield: $5.20\mathrm{g}$, 25.8%

^{1}H NMR ($400\mathrm{MHz}$, MeOH-d^4) δ (ppm)$=$ 7.94 (d, $J = 7.5$ Hz, 1 H), 7.56 (t, $J = 7.5$ Hz, 1 H), 7.46 (d, $J = 7.8$ Hz, 1H), 7.41-7.38 (m, 1 H), 7.32 (d, $J = 7.8$ Hz, 1 H), 6.99 (d, $J = 0.9$ Hz, 2 H), 6.62 (s, 1H), 6.43 (s, 1 H), 2.63-2.58 (m, 9 H), 2.14 (s, 3 H), 1.94 (s, 3 H).

^{13}C NMR ($100\mathrm{MHz}$, MeOH-d^4) δ (ppm)$=$ 145.3, 142.0, 141.5, 140.0, 139.0, 138.3, 135.6, 134.8, 133.9, 133.5, 132.6, 132.1, 131.7, 129.6, 129.5, 129.2, 128.4, 57.5, 24.5, 24.1, 20.9, 19.8, 19.3

Cristallographic data

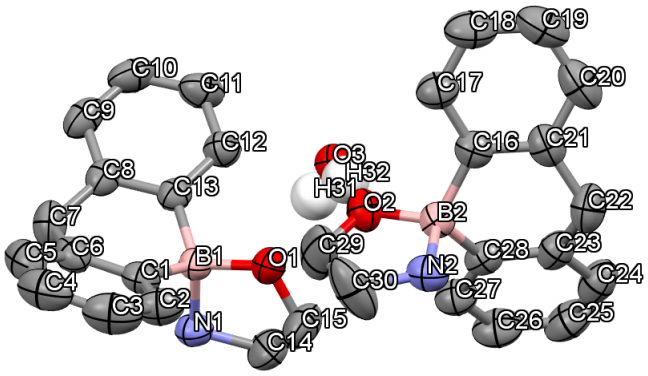
Table A.1: Cristallographic date for compounds **3**, **5**, **7**, **10**, **14**.

Compound	**3**	**5**	**7**	**10**	**14**
Formula	$2(C_{15}H_{16}BNO), H_2O$	$C_{19}H_{18}BN$	$C_{19}H_{17}BFN$	$C_{19}H_{15}BF_3N$	$C_{22}H_{21}B$
Crystal systel	orthorhombic	Monoclinic	orthorhombic	Monoclinic	Monoclinic
space group	P 2_1 2_1 2_1	C m	P b c a	P 2_1/c	P 2_1/n
Cell lengths					
a (Å)	11.42896(9)	10.2532(3)	17.4338(5)	9.41756(8)	9.08944(19)
b (Å)	11.89780(12)	16.6961(6)	9.7707(2)	11.20545(11)	8.22672(18)
c (Å)	19.5241(2)	9.2515(3)	18.1986(5)	18.07441(17)	23.3444(5)
Cell angles					
α (°)	90	90	90	90	90
β (°)	90	101.132(3)	90	102.9088(9)	94.4692(19)
γ (°)	90	90	90	90	90
Cell volume					
V (cm^3)	2654.88	1553.95	3099.96	1859.15	1740.3
Z	4	4	8	4	4
R factor (%)	3.67	3.91	4.94	4.34	4.56
T (K)	Room Temp. (283-303)	Room Temp. (283-303)	Room Temp. (283-303)	Room Temp. (283-303)	Room Temp. (283-303)

Table A.2: Cristallographic date for compounds **15**, **22**, **23**, **30**, **43**.

Compound	**15**	**22**	**23**	**30**	**43**
Formula	$C_{44}H_{40}B_2$'	$C_{19}H_{12}BF_3$	$C_{19}H_{10}BF_5$	$C_{13}H_8Br_2o_2$	$C_{23}H_{22}B^-$ $C_4H_{12}N^+$
Crystal systel	Triclinic	Triclinic	Triclinic	Orthorombic	Orthorombic
space group	P 1	P 1	P 1	P n a 2_1	P 2_1 2_1 2_1
Cell lengths					
a (Å)	8.6797(4)	8.6286(5)	7.7665(6)	14.01602(9)	9.1355(5)
b (Å)	8.9094(4)	9.4523(5)	9.5509(8)	8.81167(6)	15.2906(6)
c (Å)	12.9370(7)	10.2633(6)	11.5367(9)	19.55810(13)	16.2154(6)
Cell angles					
α (°)	92.906(4)	67.393(5)	69.971(8)	90	90
β (°)	99.390(4)	75.518(5)	77.865(7)	90	90
γ (°)	119.093(5)	79.118(5)	79.307(7)	90	90
Cell volume					
V (cm^3)	852.627	744.173	780.007	2415.51	2265.09
Z	1	2	2	8	4
R factor (%)	5.28	4.26	4.68	3.08	5.03
T (K)	Room Temp. (283-303)	Room Temp. (283-303)	Room Temp. (283-303)	Room Temp. (283-303)	100

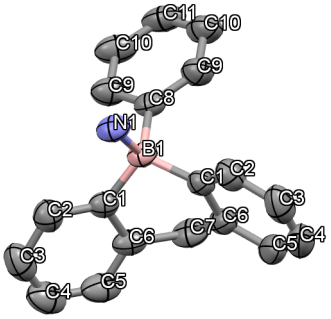
*9-aminoethoxy-9,10-dihydro-9-boraanthracene (**3**)*



Number	Label	X (Å)	Y (Å)	Z (Å)
1	O1	7.867	9.612	10.529
2	N1	9.322	10.037	8.664
3	H1A	9.855	9.381	8.384
4	H1B	9.255	10.647	8.020
5	C1	7.694	7.916	8.582
6	C2	7.948	6.832	9.403
7	H2	8.268	6.980	10.264
8	C3	7.735	5.535	8.979
9	H3	7.935	4.824	9.544
10	C4	7.231	5.290	7.728
11	H4	7.074	4.417	7.446
12	C5	6.963	6.343	6.896
13	H5	6.614	6.181	6.049
14	C6	7.203	7.657	7.300
15	C7	6.936	8.809	6.366
16	H7A	7.773	9.083	5.959
17	H7B	6.348	8.508	5.656
18	C8	6.312	10.002	7.042
19	C9	5.361	10.773	6.387
20	H9	5.098	10.541	5.525
21	C10	4.804	11.873	6.989
22	H10	4.188	12.396	6.528
23	C11	5.156	12.198	8.267
24	H11	4.763	12.929	8.685
25	C12	6.097	11.440	8.941
26	H12	6.325	11.672	9.812
27	C13	6.710	10.341	8.348
28	C14	9.847	10.643	9.909
29	H14A	10.806	10.516	9.977
30	H14B	9.653	11.593	9.938
31	C15	9.155	9.941	10.979
32	H15A	9.640	9.135	11.216
33	H15B	9.098	10.507	11.765
34	B1	7.829	9.446	9.071
35	O2	5.952	7.060	13.766

Number	Label	X (Å)	Y (Å)	Z (Å)
36	N2	6.780	5.714	15.590
37	H2A	7.567	5.801	15.997
38	H2B	6.231	5.257	16.121
39	C16	4.766	7.411	16.021
40	C17	3.517	7.093	15.500
41	H17	3.465	6.710	14.655
42	C18	2.346	7.330	16.201
43	H18	1.524	7.105	15.830
44	C19	2.408	7.904	17.452
45	H19	1.626	8.077	17.926
46	C20	3.629	8.219	17.999
47	H20	3.667	8.594	18.850
48	C21	4.807	7.987	17.301
49	C22	6.141	8.338	17.904
50	H22A	6.506	7.547	18.328
51	H22B	6.001	9.003	18.596
52	C23	7.157	8.871	16.922
53	C24	8.054	9.870	17.295
54	H24	8.021	10.219	18.157
55	C25	8.985	10.346	16.409
56	H25	9.583	11.010	16.671
57	C26	9.036	9.838	15.129
58	H26	9.658	10.165	14.520
59	C27	8.157	8.845	14.755
60	H27	8.204	8.503	13.891
61	C28	7.202	8.336	15.631
62	C29	6.477	5.870	13.278
63	H29A	7.210	6.070	12.676
64	H29B	5.793	5.405	12.772
65	C30	6.935	5.038	14.301
66	H30A	7.870	4.823	14.154
67	H30B	6.430	4.210	14.302
68	B2	6.141	7.198	15.225
69	O3	5.690	9.377	12.173
70	H31	6.400	9.459	11.679
71	H32	5.840	8.745	12.677

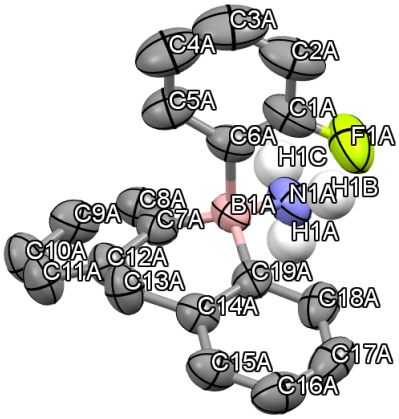
*9-phenyl-9,10-dihydro-9-boraanthracene ammoniate (**5**)*



Number	Label	X (Å)	Y (Å)	Z (Å)
1	N1	5.287	8.348	2.279
2	H1A	5.544	9.133	1.788
3	H1B	5.727	8.348	3.095
4	C1	3.310	7.056	3.440
5	C2	4.090	5.929	3.669
6	H2	4.915	5.855	3.248
7	C3	3.663	4.907	4.519
8	H3	4.213	4.171	4.667
9	C4	2.457	4.975	5.130
10	H4	2.177	4.290	5.692
11	C5	1.644	6.072	4.911
12	H5	0.809	6.115	5.318
13	C6	2.063	7.110	4.090
14	C7	1.231	8.348	3.907
15	H7A	0.842	8.348	3.019
16	H7B	0.506	8.348	4.552
17	C8	2.962	8.348	1.095
18	C9	2.626	9.522	0.439
19	H9	2.843	10.337	0.832
20	C10	1.967	9.519	-0.794
21	H10	1.750	10.325	-1.205
22	C11	1.644	8.348	-1.397
23	H11	1.203	8.348	-2.216
24	B1	3.692	8.348	2.551
25	H1A	5.544	7.563	1.788
26	C1	3.310	9.640	3.440
27	C2	4.090	10.767	3.669
28	H2	4.915	10.841	3.248
29	C3	3.663	11.789	4.519
30	H3	4.213	12.525	4.667

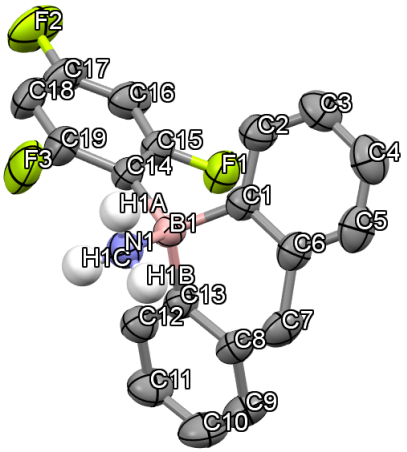
Number	Label	X (Å)	Y (Å)	Z (Å)
31	C4	2.457	11.721	5.130
32	H4	2.177	12.406	5.692
33	C5	1.644	10.624	4.911
34	H5	0.809	10.581	5.318
35	C6	2.063	9.586	4.090
36	C9	2.626	7.174	0.439
37	H9	2.843	6.359	0.832
38	C10	1.967	7.177	-0.794
39	H10	1.750	6.371	-1.205

*9-(2-fluorophenyl)-9,10-dihydro-9-boraanthracene ammoniate (**7**)*



Number	Label	X (Å)	Y (Å)	Z (Å)
1	F1A	4.221	6.661	10.562
2	C1A	5.324	7.398	10.550
3	N1A	5.584	4.771	8.861
4	H1A	5.431	4.209	8.188
5	H1B	4.848	4.849	9.355
6	H1C	6.248	4.457	9.364
7	B1A	5.996	6.231	8.266
8	C2A	5.446	8.264	11.629
9	H2A	4.795	8.316	12.291
10	C3A	6.571	9.035	11.669
11	H3A	6.692	9.634	12.370
12	C4A	7.524	8.936	10.690
13	H4A	8.277	9.480	10.724
14	C5A	7.376	8.041	9.660
15	H5A	8.051	7.970	9.025
16	C6A	6.241	7.232	9.536
17	C7A	7.307	6.061	7.356
18	C8A	8.240	5.025	7.445
19	H8A	8.117	4.371	8.094
20	C9A	9.349	4.929	6.601
21	H9A	9.954	4.229	6.691
22	C10A	9.528	5.896	5.630
23	H10A	10.263	5.854	5.062
24	C11A	8.621	6.918	5.507
25	H11A	8.747	7.562	4.849
26	C12A	7.520	7.009	6.346
27	C13A	6.538	8.141	6.184
28	H13A	6.759	8.837	6.822
29	H13B	6.639	8.515	5.295
30	C14A	5.108	7.745	6.379

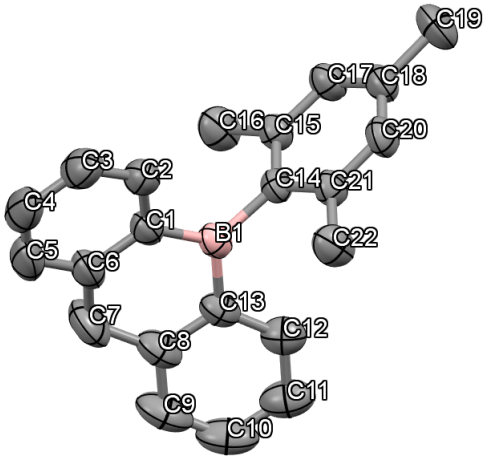
Number	Label	X (Å)	Y (Å)	Z (Å)
31	C15A	4.113	8.325	5.595
32	H15A	4.339	8.957	4.952
33	C16A	2.804	7.966	5.767
34	H16A	2.145	8.360	5.243
35	C17A	2.460	7.040	6.699
36	H17A	1.570	6.792	6.804
37	C18A	3.434	6.466	7.491
38	H18A	3.184	5.839	8.129
39	C19A	4.783	6.796	7.363



Number	Label	X (Å)	Y (Å)	Z (Å)
1	F1	-0.211	1.384	12.745
2	N1	1.047	5.604	12.391
3	H1A	1.470	5.639	11.594
4	H1B	1.583	5.949	13.032
5	H1C	0.282	6.082	12.348
6	B1	0.699	4.058	12.753
7	C1	2.135	3.320	12.780
8	F2	-2.960	1.562	9.001
9	C2	2.688	2.646	11.688
10	H2	2.188	2.573	10.907
11	C3	3.953	2.085	11.725
12	H3	4.288	1.634	10.985
13	F3	-0.693	5.405	10.368
14	C9	0.362	4.108	16.635
15	H9	0.937	4.122	17.365
16	C4	4.711	2.201	12.869
17	H4	5.570	1.844	12.899
18	C5	4.194	2.847	13.967
19	H5	4.707	2.915	14.740
20	C7	2.387	4.108	15.168
21	H7A	2.795	3.706	15.951
22	H7B	2.674	5.034	15.133
23	C6	2.913	3.401	13.942
24	C8	0.889	4.080	15.345
25	C10	-0.997	4.115	16.840
26	H10	-1.339	4.141	17.705
27	C11	-1.845	4.083	15.764
28	H11	-2.765	4.082	15.897
29	C12	-1.330	4.052	14.477
30	H12	-1.918	4.025	13.757

Number	Label	X (Å)	Y (Å)	Z (Å)
31	C13	0.042	4.059	14.230
32	C14	-0.331	3.449	11.636
33	C15	-0.720	2.121	11.722
34	C16	-1.585	1.453	10.884
35	H16	-1.794	0.555	11.008
36	C17	-2.116	2.179	9.864
37	C18	-1.835	3.495	9.681
38	H18	-2.219	3.982	8.988
39	C19	-0.950	4.079	10.573

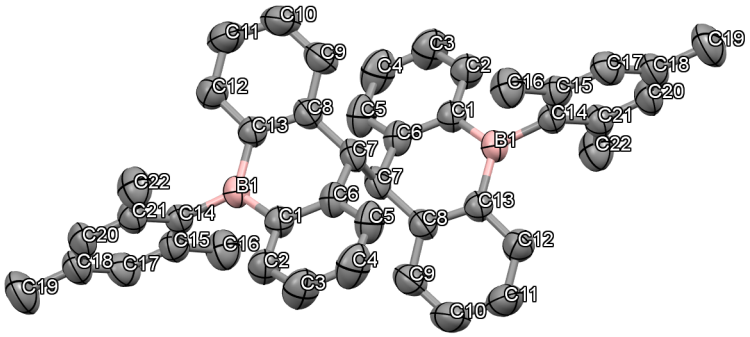
*9-mesityl-9,10-dihydro-9-boraanthracene (**14**)*



Number	Label	X (Å)	Y (Å)	Z (Å)
1	C1	3.025	5.062	16.418
2	C2	1.772	5.589	16.757
3	H2	1.297	6.073	16.120
4	C3	1.224	5.410	18.006
5	H3	0.403	5.791	18.220
6	C4	1.911	4.654	18.944
7	H4	1.545	4.518	19.788
8	C5	3.123	4.108	18.635
9	H5	3.565	3.591	19.269
10	C6	3.708	4.310	17.391
11	C7	5.039	3.693	17.080
12	H7A	5.587	3.749	17.878
13	H7B	4.895	2.751	16.897
14	C8	5.827	4.267	15.941
15	C9	7.197	4.024	15.844
16	H9	7.616	3.509	16.495
17	C10	7.935	4.529	14.811
18	H10	8.850	4.363	14.773
19	C11	7.335	5.281	13.825
20	H11	7.842	5.630	13.128
21	C12	5.980	5.510	13.882
22	H12	5.574	6.000	13.204
23	C13	5.197	5.025	14.935
24	C14	2.849	5.871	13.826
25	C15	2.200	4.956	12.992
26	C16	2.346	3.473	13.228
27	H16A	3.225	3.192	12.966
28	H16B	1.691	3.001	12.708
29	H16C	2.213	3.283	14.160
30	C17	1.428	5.413	11.933

Number	Label	X (Å)	Y (Å)	Z (Å)
31	H17	0.999	4.793	11.389
32	C18	1.276	6.755	11.665
33	C19	0.408	7.202	10.502
34	H19A	0.701	6.767	9.698
35	H19B	0.481	8.153	10.396
36	H19C	-0.507	6.969	10.677
37	C20	1.932	7.653	12.479
38	H20	1.849	8.564	12.307
39	C21	2.717	7.236	13.552
40	C22	3.414	8.248	14.417
41	H22A	3.079	8.187	15.315
42	H22B	3.250	9.130	14.074
43	H22C	4.358	8.075	14.416
44	B1	3.685	5.327	15.048

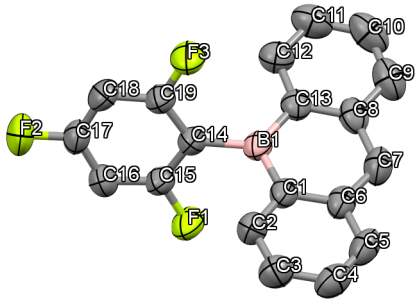
*9-mesityl-9,10-dihydro-9-boraanthracene dimer (**15**)*



Number	Label	X (Å)	Y (Å)	Z (Å)
1	C1	3.689	4.072	2.405
2	C2	4.852	4.555	3.020
3	H2	5.270	4.039	3.671
4	C3	5.390	5.778	2.683
5	H3	6.167	6.079	3.096
6	C4	4.770	6.546	1.731
7	H4	5.119	7.380	1.514
8	C5	3.636	6.097	1.093
9	H5	3.234	6.627	0.444
10	C6	3.085	4.863	1.407
11	C7	1.917	4.325	0.625
12	H7	1.415	5.090	0.274
13	C8	0.970	3.503	1.478
14	C9	-0.393	3.499	1.220
15	H9	-0.734	4.047	0.550
16	C10	-1.247	2.700	1.941
17	H10	-2.157	2.709	1.751
18	C11	-0.766	1.885	2.937
19	H11	-1.348	1.348	3.424
20	C12	0.585	1.872	3.210
21	H12	0.907	1.318	3.883
22	C13	1.485	2.677	2.496
23	C14	3.691	1.693	3.782
24	C15	4.250	0.549	3.186
25	C16	4.185	0.353	1.704
26	H16A	3.272	0.402	1.414
27	H16B	4.547	-0.507	1.479
28	H16C	4.697	1.039	1.268
29	C17	4.860	-0.417	3.985
30	H17	5.218	-1.173	3.579
31	C18	4.950	-0.290	5.351
32	C19	5.609	-1.351	6.204
33	H19A	6.057	-0.934	6.944
34	H19B	6.249	-1.834	5.675
35	H19C	4.942	-1.957	6.533

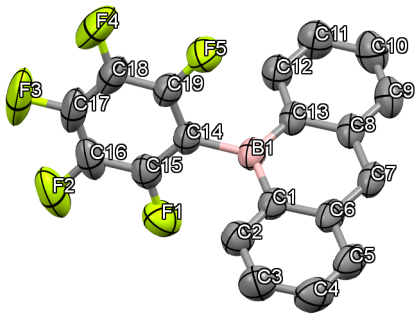
Number	Label	X (Å)	Y (Å)	Z (Å)
36	C20	4.397	0.836	5.926
37	H20	4.438	0.936	6.850
38	C21	3.779	1.827	5.171
39	C22	3.183	3.024	5.869
40	H22A	3.788	3.766	5.803
41	H22B	3.034	2.814	6.794
42	H22C	2.348	3.253	5.454
43	B1	2.977	2.781	2.888
44	C1	0.658	3.713	-2.405
45	C2	-0.504	3.230	-3.020
46	H2	-0.923	3.747	-3.671
47	C3	-1.042	2.008	-2.683
48	H3	-1.819	1.707	-3.096
49	C4	-0.422	1.240	-1.731
50	H4	-0.772	0.405	-1.514
51	C5	0.712	1.689	-1.093
52	H5	1.114	1.158	-0.444
53	C6	1.262	2.922	-1.407
54	C7	2.431	3.460	-0.625
55	H7	2.933	2.696	-0.274
56	C8	3.377	4.282	-1.478
57	C9	4.741	4.286	-1.220
58	H9	5.082	3.738	-0.550
59	C10	5.595	5.086	-1.941
60	H10	6.505	5.076	-1.751
61	C11	5.114	5.900	-2.937
62	H11	5.696	6.438	-3.424
63	C12	3.763	5.913	-3.210
64	H12	3.441	6.468	-3.883
65	C13	2.863	5.108	-2.496
66	C14	0.657	6.092	-3.782
67	C15	0.098	7.236	-3.186
68	C16	0.162	7.433	-1.704
69	H16A	1.076	7.383	-1.414
70	H16B	-0.199	8.293	-1.479
71	H16C	-0.349	6.747	-1.268
72	C17	-0.513	8.203	-3.985
73	H17	-0.871	8.959	-3.579
74	C18	-0.603	8.075	-5.351
75	C19	-1.261	9.136	-6.204
76	H19A	-1.709	8.719	-6.944
77	H19B	-1.901	9.620	-5.675
78	H19C	-0.595	9.743	-6.533
79	C20	-0.049	6.949	-5.926
80	H20	-0.090	6.850	-6.850
81	C21	0.569	5.958	-5.171
82	C22	1.164	4.762	-5.869
83	H22A	0.560	4.019	-5.803
84	H22B	1.313	4.972	-6.794
85	H22C	1.999	4.532	-5.454
86	B1	1.370	5.004	-2.888

*9-(2,4,6-trifluorophenyl)-9,10-dihydro-9-boraanthracene (**22**)*



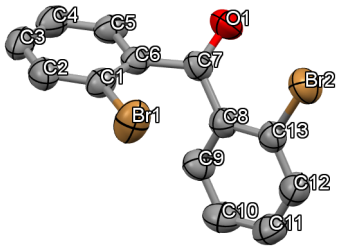
Number	Label	X (Å)	Y (Å)	Z (Å)
1	F1	5.139	5.495	4.314
2	F3	4.508	6.654	8.790
3	F2	2.402	9.103	5.419
4	C19	4.276	6.860	7.462
5	C1	5.352	3.346	6.707
6	C14	4.884	5.999	6.575
7	C13	7.216	5.007	7.582
8	C18	3.439	7.900	7.129
9	H18	3.053	8.447	7.775
10	C8	8.070	3.897	7.746
11	C2	4.044	3.041	6.298
12	H2	3.426	3.730	6.204
13	C6	6.259	2.285	6.869
14	C5	5.845	0.982	6.571
15	H5	6.450	0.281	6.654
16	C15	4.573	6.283	5.253
17	C12	7.690	6.274	7.973
18	H12	7.144	7.017	7.857
19	C16	3.758	7.297	4.821
20	H16	3.589	7.442	3.917
21	C4	4.575	0.722	6.161
22	H4	4.324	-0.152	5.967
23	C3	3.654	1.749	6.033
24	H3	2.781	1.566	5.769
25	C17	3.210	8.084	5.794
26	C9	9.338	4.089	8.287
27	H9	9.907	3.360	8.387
28	C7	7.662	2.521	7.323
29	H7A	8.252	2.249	6.603
30	H7B	7.831	1.924	8.069
31	B1	5.822	4.785	6.974
32	C11	8.940	6.439	8.522
33	H11	9.230	7.282	8.788
34	C10	9.762	5.330	8.673
35	H10	10.610	5.433	9.041

*9-(pentafluorophenyl)-9,10-dihydro-9-boraanthracene (**23**)*



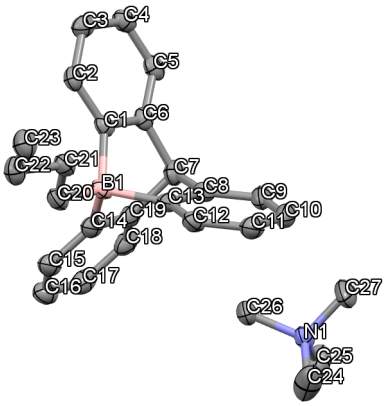
Number	Label	X (Å)	Y (Å)	Z (Å)
1	B1	4.823	9.437	6.899
2	C1	4.328	8.973	5.525
3	F1	2.553	8.235	8.269
4	C2	3.890	7.667	5.256
5	H2	3.908	7.037	5.941
6	F2	2.706	6.445	10.267
7	C3	3.434	7.290	4.018
8	H3	3.156	6.416	3.864
9	F3	5.126	5.680	11.219
10	C4	3.395	8.226	3.007
11	H4	3.073	7.983	2.169
12	F4	7.407	6.725	10.148
13	C5	3.826	9.507	3.219
14	H5	3.799	10.121	2.521
15	F5	7.249	8.472	8.140
16	C6	4.305	9.905	4.469
17	C7	4.803	11.307	4.641
18	H7A	5.527	11.440	4.009
19	H7B	4.086	11.906	4.381
20	C8	5.291	11.748	5.983
21	C9	5.778	13.039	6.130
22	H9	5.792	13.608	5.394
23	C10	6.238	13.490	7.337
24	H10	6.573	14.354	7.410
25	C11	6.206	12.665	8.451
26	H11	6.504	12.978	9.275
27	C12	5.733	11.384	8.326
28	H12	5.710	10.835	9.076
29	C13	5.280	10.878	7.098
30	C14	4.892	8.401	8.112
31	C15	3.767	7.853	8.699
32	C16	3.825	6.947	9.735
33	C17	5.053	6.565	10.212
34	C18	6.197	7.080	9.672
35	C19	6.099	7.981	8.642

*2,2'-dibromobenzophenone (**30**)*



Number	Label	X (Å)	Y (Å)	Z (Å)
1	Br1	12.299	3.602	4.939
2	Br2	8.507	3.219	6.846
3	O1	10.470	5.236	8.261
4	C1	13.197	4.749	6.155
5	C2	14.369	5.351	5.729
6	H2	14.722	5.158	4.889
7	C3	15.008	6.245	6.570
8	H3	15.803	6.647	6.299
9	C4	14.486	6.539	7.784
10	H4	14.932	7.134	8.343
11	C5	13.290	5.963	8.207
12	H5	12.930	6.191	9.033
13	C6	12.634	5.040	7.387
14	C7	11.331	4.479	7.876
15	C8	11.162	3.001	7.948
16	C9	12.236	2.235	8.430
17	H9	13.039	2.653	8.642
18	C10	12.118	0.871	8.592
19	H10	12.844	0.377	8.901
20	C11	10.947	0.242	8.302
21	H11	10.865	-0.674	8.433
22	C12	9.880	0.968	7.813
23	H12	9.087	0.530	7.599
24	C13	9.968	2.316	7.639

*9-nbutyl-9-boratriptycene tetramethylamminium salt (**43**)*



Number	Label	X (Å)	Y (Å)	Z (Å)
1	B1	5.400	7.930	9.108
2	C1	3.847	7.456	9.397
3	C2	3.306	6.174	9.359
4	H2	3.853	5.446	9.086
5	C3	1.970	5.934	9.715
6	H3	1.621	5.050	9.685
7	C4	1.159	6.988	10.112
8	H4	0.265	6.824	10.387
9	C5	1.658	8.280	10.105
10	H5	1.099	9.008	10.351
11	C6	2.975	8.509	9.738
12	C7	3.625	9.895	9.694
13	H7	2.970	10.619	9.908
14	C8	4.763	9.846	10.702
15	C9	4.844	10.671	11.815
16	H9	4.163	11.312	11.983
17	C10	5.928	10.558	12.687
18	H10	5.984	11.117	13.452
19	C11	6.916	9.633	12.436
20	H11	7.659	9.561	13.022
21	C12	6.827	8.797	11.315
22	H12	7.522	8.171	11.149
23	C13	5.738	8.859	10.431
24	C14	5.183	9.083	7.961
25	C15	5.751	9.167	6.699
26	H15	6.377	8.505	6.429
27	C16	5.432	10.196	5.813
28	H16	5.853	10.239	4.962
29	C17	4.498	11.156	6.176
30	H17	4.274	11.854	5.572
31	C18	3.889	11.095	7.432
32	H18	3.245	11.747	7.683
33	C19	4.232	10.072	8.311
34	C20	6.444	6.765	8.724
35	H20A	6.129	6.341	7.887

Number	Label	X (Å)	Y (Å)	Z (Å)
36	H20B	7.314	7.193	8.524
37	C21	6.701	5.639	9.750
38	H21A	7.177	6.020	10.530
39	H21B	5.830	5.293	10.069
40	C22	7.520	4.476	9.189
41	H22A	6.984	4.011	8.499
42	H22B	8.329	4.838	8.748
43	C23	7.951	3.457	10.242
44	H23A	8.380	2.694	9.801
45	H23B	7.165	3.148	10.738
46	H23C	8.585	3.875	10.860
47	N1	5.614	14.601	10.315
48	C24	7.097	14.681	10.485
49	H24A	7.430	13.835	10.850
50	H24B	7.317	15.411	11.100
51	H24C	7.517	14.849	9.615
52	C25	5.152	15.876	9.734
53	H25A	5.558	16.000	8.851
54	H25B	5.414	16.617	10.321
55	H25C	4.176	15.860	9.645
56	C26	5.261	13.466	9.405
57	H26A	4.288	13.425	9.297
58	H26B	5.582	12.625	9.792
59	H26C	5.681	13.605	8.531
60	C27	4.975	14.399	11.631
61	H27A	4.007	14.299	11.514
62	H27B	5.155	15.175	12.204
63	H27C	5.339	13.592	12.052

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